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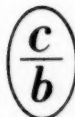
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## SPECTROPHOTOMETRIC INVESTIGATION OF COBALT-

### (II)-HALIDE COMPLEXES IN SOLUTIONS OF PROPYL ALCOHOL

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Cobalt halides have long been of interest because of their capability of changing color in solutions, depending upon the solvent or the excess of halide ions.

Spectroscopic investigations have established that the change in color of cobalt halides in aqueous solutions with excess of halide ions, and also in nonaqueous solution, coincide with the absorption maximum in the spectral region 660-700 m [1]. The theory of complex compounds explains this by the formation of the complexes  $\text{CoCl}_4^{--}$ ,  $\text{CoBr}_4^{--}$ ,  $\text{CoI}_4^{--}$ . The hydrate theory considers the cause of this phenomenon to be the formation of solvates of the type:  $\text{CoR}_2\text{Cl}_2$ ;  $\text{CoR}_2\text{Br}_2$  and  $\text{CoR}_2\text{I}_2$ .

Ganch, having obtained crystals of the type:  $\text{CoR}_2\text{H}_2$ ;  $\text{CoR}_4\text{H}_2$ ;  $\text{CoR}_6\text{H}_2$ ,  
blue red rose

(R - molecule of solvent; H - halide ion), in a series of solvents including alcohols, came to the conclusion that in these solvents complexes of the type  $\text{CoH}_4^{--}$  were not present, since upon increasing the number of addendas the color changed from blue to rose. We attempted to determine the composition of the cobalt halide complexes in solutions of propyl alcohol by the method of continuous change.

#### EXPERIMENTAL

Chemically pure  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  served as the source of cobalt since the  $\text{ClO}_4^-$  ion does not have any influence on the absorption in the region of 600-700 m $\mu$ . The cobalt perchlorate was prepared from chemically pure cobalt carbonate, free from nickel, and a solution of chemically pure perchloric acid. The chemically pure propyl alcohol (normal) was dehydrated with metallic potassium. The optical density was measured by a Beckman spectrophotometer at a temperature of  $20^\circ \pm 1^\circ$ .

As a result of the investigation diagrams were constructed showing composition -  $\bar{D}$ . The composition was expressed in molar concentrations and placed on the abscissa.  $\bar{D}$  was determined from the equation  $\bar{D} = D - (D_1 + D_2)$ , where D - optical density of the solution  $\text{Co}(\text{ClO}_4)_2 + \text{LiHal}$ , prepared from a mixture of the solutions  $\text{Co}(\text{ClO}_4)_2 + \text{LiHal}$ ;  
 $D_1$ - optical density of the solution  $\text{Co}(\text{ClO}_4)_2$ ;  
 $D_2$ - optical density of the solution  $\text{LiHal}$ .

The presence of maxima or minima on the curve, composition -  $\bar{D}$ , indicates the presence of a complex in the solution and its composition [2].

### Cobalt-(II)-Chloride Complexes

The absorption spectra of solutions of cobalt chloride in propyl alcohol show a strong absorption in the region of 600-700 mμ.

To establish the composition of cobalt-(II)-chloride complexes we investigated the system  $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$  in propyl alcohol.

The lithium chloride was prepared from lithium carbonate and chemically pure hydrochloric acid. The doubly recrystallized  $\text{LiCl}$  was dehydrated at  $112^\circ$  in a current of nitrogen. For the measurement of the optical density a mixture

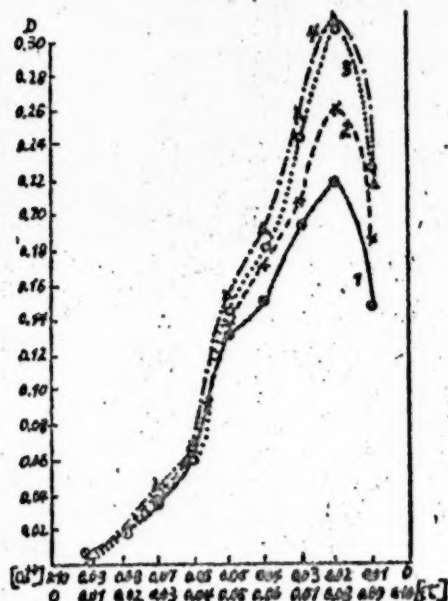


Fig. 1. Cobalt perchlorate + Lithium Chloride.

1 -  $\lambda=600$ ; 2 -  $\lambda=625$ ; 3 -  $\lambda=675$ ; 4 -  $\lambda=650$

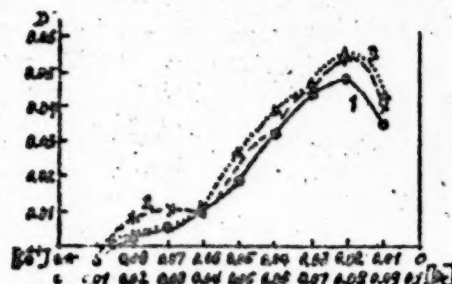


Fig. 2. Cobalt Perchlorate + Lithium Chloride

1 -  $\lambda=625$ ; 2 -  $\lambda=650$ ; 3 -  $\lambda=675$

of cobalt perchlorate and lithium chloride solutions in propyl alcohol were prepared in a volume of 5 ml with a concentration of 0.1 mol/l.

The details for the preparation of the solutions are seen in Table 1, in which are given the composition of the solutions and their corresponding optical density. The curve, composition -  $\bar{D}$ , is shown in Fig. 1. As is evident from Fig. 1, this curve has a maximum at the composition  $\text{Co}(\text{ClO}_4)_2$  0.02 mol/l. and  $\text{LiCl}$  0.08 mol/l., which indicates the existence of the complex  $\text{CoCl}_4^{--}$ .

The maximum absorption of the  $\text{CoCl}_4^{--}$  complexes lies in the region 600-675 mμ.

### Cobalt-(II)-Bromide Complexes

The presence of complexes in solutions of cobalt bromide in propyl alcohol may be postulated on the basis of the molecular weight determination of cobalt bromide in solutions of  $\text{CoBr}_2$  in ethyl alcohol and our spectrophotometric investigations of cobalt-(II)-bromide complexes in ethyl alcohol.

The determined molecular weight of cobalt bromide in ethyl alcohol was equal to 230.3; theoretically, corresponding to the formula  $\text{CoBr}_2$ , it is equal to 218.89. Our spectrophotometric investigations of  $\text{Co}(\text{ClO}_4)_2 + \text{LiBr}$  solutions in ethyl alcohol indicated the presence of  $\text{CoBr}_4^{--}$  complexes in these solutions. To establish the composition of the cobalt-(II)-bromide complexes in solutions



of propyl alcohol, the system  $\text{Co}(\text{ClO}_4)_2 + \text{LiBr}$  was investigated by the method of continuous change.

TABLE 1

$\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$  in Propyl Alcohol

Exp. No.	Composition of solutions				Optical density at $\lambda$ (in $\text{m}\mu$ )				$\bar{D}$ at $\lambda$ (in $\text{m}\mu$ )			
	in ml		Con. (mol/l.)									
	$\text{Co}(\text{ClO}_4)_2$	$\text{LiCl}$	$\text{Co}(\text{ClO}_4)_2$	$\text{LiCl}$	600	625	650	675	600	625	650	675
1	4.5	0.5	0.09	0.01	0.054	0.044	0.040	0.031				
	4.5	—	0.09	—	0.047	0.040	0.035	0.026	0.007	0.004	0.005	0.004
2	4.0	1.0	0.08	0.02	0.060	0.054	0.050	0.043				
	4.0	—	0.08	—	0.042	0.035	0.031	0.024	0.018	0.019	0.019	0.019
3	3.5	1.5	0.07	0.03	0.073	0.072	0.072	0.060				
	3.5	—	0.07	—	0.037	0.032	0.028	0.023	0.036	0.040	0.044	0.037
4	3.0	2.0	0.06	0.04	0.090	0.086	0.090	0.078				
	3.0	—	0.06	—	0.031	0.026	0.023	0.018	0.059	0.060	0.067	0.060
5	2.5	2.5	0.05	0.05	0.156	0.160	0.172	0.160				
	2.5	—	0.05	—	0.025	0.023	0.019	0.015	0.131	0.137	0.153	0.145
6	2.0	3.0	0.04	0.06	0.170	0.188	0.206	0.192				
	2.0	—	0.04	—	0.020	0.018	0.015	0.011	0.150	0.170	0.191	0.181
7	1.5	3.5	0.03	0.07	0.210	0.240	0.270	0.255				
	1.5	—	0.03	—	0.016	0.014	0.013	0.010	0.194	0.226	0.257	0.245
8	1.0	4.0	0.02	0.008	0.230	0.270	0.320	0.315				
	1.0	—	0.02	—	0.011	0.009	0.008	0.008	0.219	0.261	0.312	0.307
9	0.5	4.5	0.01	0.009	0.155	0.190	0.222	0.230				
	0.5	—	0.01	—	0.006	0.005	0.004	0.003	0.149	0.185	0.218	0.227

TABLE 2

$\text{Co}(\text{ClO}_4)_2 + \text{LiBr}$  in Propyl Alcohol

Exp. No.	Composition of solutions				Optical density at $\lambda$ (in $\text{m}\mu$ )			$\bar{D}$ at $\lambda$ (in $\text{m}\mu$ )		
	(in ml)		Con. in mol/l)							
	$\text{Co}(\text{ClO}_4)_2$	$\text{LiBr}$	$\text{Co}(\text{ClO}_4)_2$	$\text{LiBr}$	625	650	675	625	650	675
1	4.5	0.5	0.09	0.01	0.036	0.033	0.025	0.004	0.002	0.001
	4.5	—	0.09	—	0.040	0.035	0.026			
2	4.0	1.0	0.08	0.02	0.038	0.040	0.028	0.003	0.009	0.004
	4.0	—	0.08	—	0.035	0.031	0.024			
3	3.5	1.5	0.07	0.03	0.037	0.039	0.028	0.005	0.011	0.005
	3.5	—	0.07	—	0.032	0.028	0.023			
4	3.0	2.0	0.06	0.04	0.038	0.033	0.030	0.012	0.010	0.010
	3.0	—	0.06	—	0.026	0.023	0.018			
5	2.5	2.5	0.05	0.05	0.042	0.043	0.042	0.019	0.024	0.027
	2.5	—	0.05	—	0.023	0.019	0.015			
6	2.0	3.0	0.04	0.06	0.051	0.049	0.050	0.033	0.034	0.039
	2.0	—	0.04	—	0.018	0.015	0.011			
7	1.5	3.5	0.03	0.07	0.057	0.058	0.057	0.043	0.045	0.047
	1.5	—	0.03	—	0.014	0.013	0.010			
8	1.0	4.0	0.02	0.08	0.057	0.062	0.063	0.048	0.054	0.055
	1.0	—	0.02	—	0.009	0.008	0.008			
9	0.5	4.5	0.01	0.009	0.040	0.045	0.046	0.035	0.040	0.043
	0.5	—	0.01	—	0.005	0.005	0.003			

For measuring the optical density, solutions were prepared by mixing 0.1 M solutions of  $\text{Co}(\text{ClO}_4)_2$  and 0.1 M solutions of lithium bromide in propyl alcohol. The total concentration of each solution so prepared was equal to 0.1 M, and the volume of the solution was equal to 5 ml. Details for the preparation of the solutions are evident from Table 2, where the compositions of the solutions and their optical densities are presented.

The curve for composition -  $\bar{D}$  is presented in Fig. 2.

The maximum on the curve  $\bar{D}$  - composition corresponds to 0.02 M  $\text{Co}(\text{ClO}_4)_2$  and 0.08 M LiBr, which corresponds to the complex  $\text{CoBr}_4^-$ . The maximum absorption of the cobalt-(II) bromide complexes lies in the region of 625-675 m $\mu$ .

### Cobalt-(II)-Iodide Complexes

The existence of cobalt iodide complexes in solutions of propyl alcohol may be postulated on the basis of their presence in solutions of  $\text{CoI}_2$  in ethyl

alcohol. Besides, spectral investigations on the absorption of aqueous solutions of cobalt iodide in concentrated hydriodic acid showed a complete analogy to aqueous solutions of  $\text{CoCl}_2$  in concentrated solutions of hydrochloric acid with the difference that the absorption of solutions in  $\text{CoI}_2$  was shifted towards the lower portion. The composition of the cobalt-(II) iodide complexes was determined analogously to cobalt-(II)-chloride and bromide.

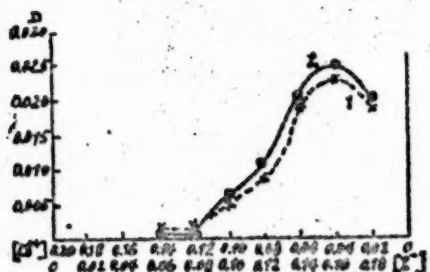


Fig. 3. Cobalt Perchlorate + Lithium Iodide

1-  $\lambda=700$ ; 2-  $\lambda=675$

The system  $\text{Co}(\text{ClO}_4)_2 + \text{LiI}$  was investigated in propyl alcohol. The concentration of the solutions was increased to 0.2 mol/l., since for

TABLE 3

$\text{Co}(\text{ClO}_4)_2 + \text{LiI}$  in Propyl Alcohol

Exp. No.	Composition of solutions				Optical density at		$\bar{D}$ at $\lambda$ (in m $\mu$ )	
	in ml		Conc. in mol/l.		$\lambda$ (in m $\mu$ )		675	700
	$\text{Co}(\text{ClO}_4)_2$	LiI	$\text{Co}(\text{ClO}_4)_2$	LiI	675	700		
1	4.5	0.5	0.18	0.02	0.050	0.035	0.000	0.000
	4.5	—	0.18	—	0.050	0.035		
2	4.0	1.0	0.16	0.04	0.046	0.031	0.000	0.000
	4.0	—	0.16	—	0.046	0.031		
3	3.5	1.5	0.14	0.028	0.041	0.028	0.001	0.001
	3.5	—	0.14	—	0.040	0.027		
4	3.0	2.0	0.12	0.008	0.037	0.027	0.001	0.002
	3.0	—	0.12	—	0.036	0.025		
5	2.5	2.5	0.10	0.10	0.038	0.028	0.007	0.006
	2.5	—	0.10	—	0.031	0.022		
6	2.0	3.0	0.08	0.12	0.037	0.029	0.011	0.009
	2.0	—	0.08	—	0.026	0.020		
7	1.5	3.5	0.06	0.14	0.039	0.033	0.021	0.019
	1.5	—	0.06	—	0.018	0.014		
8	1.0	4.0	0.04	0.16	0.038	0.034	0.025	0.023
	1.0	—	0.04	—	0.013	0.011		
9	0.5	4.5	0.02	0.18	0.028	0.025	0.020	0.019
	0.5	—	0.02	—	0.008	0.006		

0.2 M solution the value for  $\bar{D}$  lay within limits close to errors of measurement. The composition of the solutions and their corresponding optical densities are shown in Table 3. The curve, Composition -  $\bar{D}$ , is presented in Fig. 3.

The maximum on the curve corresponds to the composition 0.04 M  $\text{Co}(\text{ClO}_4)_2$  and 0.016 M LiI, which corresponds to the complex  $\text{CoI}_4^-$ . The maximum absorption of the  $\text{CoI}_4^-$  complexes lies in the region of 675-700 m $\mu$ .

#### SUMMARY

1. With the aid of spectrophotometric measurements the following systems were investigated:  $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$ ;  $\text{Co}(\text{ClO}_4)_2 + \text{LiBr}$ ; and  $\text{Co}(\text{ClO}_4)_2 + \text{LiI}$  in propyl alcohol.

2. By the method of continuous change it was established that in 0.1 solutions of propyl alcohol complexes were present in which the ratio of cobalt ions and chlorine ions, as well as cobalt ions and bromine ions was equal to 1:4. The same ratio between the ions of cobalt and iodine was found in 0.2 M solutions of  $\text{Co}(\text{ClO}_4)_2 + \text{LiI}$  in propyl alcohol.

3. The maximum absorption of the cobalt halide complexes in propyl alcohol was found in the spectral region of 625-700 m $\mu$ .

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# CHEMICAL REACTIONS OF INTERMETALLIC PHASES

## I. DISINTEGRATION OF THE INTERMETALLIC COMPOUNDS $Ag_5Al_3$ and $Mg_2Pb$

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In the preparation of a series of special alloys, in practice the technology of these alloys requires the preparation of a base-alloy. Intermetallic phases enter into the composition of such base-alloys, and include several metallic compounds.

Industrial and laboratory practice frequently indicates that a base-alloy, a short time after its preparation, is very strongly corroded and crumbles into a powder even in the absence of reactive chemical substances. There are well known instances of the disintegration of special base-alloys, necessary for the preparation of commercial alloys and also alloys for purposes of scientific investigation.

In 1935 Tamman [1] made generalizations based on extensive experimental material, all observations on the chemical instability of intermetallic compounds being made under ordinary atmospheric conditions. Analysis of this material permitted Tamman to express the following postulation on the nature of the processes taking place in the disintegration of intermetallic compounds.

- 1) the chemical decomposition of intermetallic compounds takes place in a medium containing water vapor.
- 2) the products of corrosion of the metals are metallic oxides and hydroxides; the corrosion process consists of the dislodgement of hydrogen from water by the metal.
- 3) the chemical activity of intermetallic compounds is influenced by the position of the components in the electromotive series. The closest metals in the electromotive series form compounds which do not undergo extensive chemical corrosion. Where pairs of metals are formed in which one component is an inert metal, a protective action takes place.

Table 1 illustrates these conclusions.

Table 1

1	2								
Al	Mg	<u>Mn</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Sb</u>	Cu	Ag	Au
Mg	Al	Zn	<u>Cd</u>	<u>Pb</u>	<u>Sn</u>	<u>Sb</u>	Cu	Ag	Au

In the first group are shown metals forming a series of metallic compounds with metals of the second group. The latter are placed in electromotive order and several are underlined which indicates that the corresponding metallic compounds are capable of being subjected to 'spontaneous' chemical disintegration.



We have called this phenomenon a "spontaneous" chemical disintegration in view of the fact that the latter takes place without the presence of active chemical reagents (in the usual sense of the word) and caused a rapid decomposition of the intermetallic phases into a finely-dispersed powder under ordinary atmospheric conditions.

The above-described phenomenon is of practical as well as of theoretical interest. The investigation of this phenomenon is necessary for practical reasons because the "spontaneous" disintegration of the alloy is unsuitable for proper alloy production and for theoretical reasons because the determination of the nature of the increased activity of the intermetallic compounds is of metallographic interest.

In a study of silver-aluminum alloys undertaken for the past several years at the metallographic laboratory of the Gorky Institute of Chemistry of Kharkov State University, a phenomenon was discovered reminiscent of this "spontaneous" process of chemical disintegration, although from Tamman's table (Table 1) it follows that a corrosive disintegration should not take place in this case in view of the presence of a protective action.

The "spontaneous" decomposition in air of the  $\gamma$ -phase [2] including the intermetallic compound  $\text{Ag}_5\text{Al}_3$  (the  $\epsilon$ -phase according to the Hume-Rothery classification [3]), led to great difficulties in the investigation of the system Ag - Al, especially in the preparation of these alloys. This induced us to study this phenomenon.

We also studied the decomposition kinetics of the Mg - Pb alloys. The investigation of the decomposition in air of Mg - Pb alloys of various compositions as a function of time enabled us to make a series of theoretical and practical conclusions.

Actually the investigation of the chemical reactions of the intermetallic phases arises from the necessity of studying the corrosion processes of industrial alloys. The scientific development of methods to fight corrosion cannot dispense with the investigation of all metallic systems including those not having any special practical significance at the present time. In this regard the chemical and electrochemical properties of intermetallic phases with metallic compounds have been studied least, which has also been noted by G.V. Akimov in his comprehensive work, "Theory and Methods of Investigation of the Corrosion of Metals" [4].

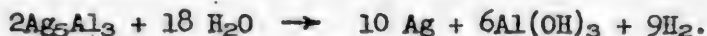
#### 1. "Spontaneous" Disintegration of the $\gamma$ -Phase Ag - Al

For the investigation of the decomposition of the  $\gamma$ -phase containing the intermetallic compound  $\text{Ag}_5\text{Al}_3$ , alloys were prepared containing 87% Ag and 13% Al under different conditions of smelting.

The smelting conditions, and their influence on the decomposition of the alloy is given in Table 2.

As is evident from the results of the investigation (Table 2), only those alloys of the  $\gamma$ -region corrode strongly which were smelted under the hygroscopic slag  $\text{CaCl}_2 + \text{NaCl}$ .

The intermetallic compound reacts with the water vapor of the atmosphere according to the reaction:



In the second experiment the alloy was denser and since a smaller quantity of the hygroscopic slag was entrapped, it corroded to a smaller degree.

In the absence of moisture alloys do not corrode.

It is to be especially noted that the method of smelting in experiment No. 2 gave a higher quality alloy. Here the components were melted in the usual manner, the melt cooled, using a thermocouple, to below the liquidus temperature until crystals appeared and then melted anew closely applying the maximum permissible heating above the liquidus line, from which the final cooling and crystallization were produced. In our case it was experimentally established that the densest alloy was obtained upon heating not over 20-30° and where this temperature was approached from below, double crystallization was obtained. We applied such a method of smelting for the preparation of samples for electroconductivity, according to the method of Stepanova [2,6]. This method of smelting may be recommended for the laboratory for purposes of scientific investigation and may also be studied for application in special cases of industrial practice.

Table 2

Exp. No.	Conditions of Alloy Smelting	Corrosion conditions	Result
1	Under a slag of $\text{CaCl}_2 + \text{NaCl}$ . Heated 200-300° over the liquidus temp. Cooled slowly. Alloy was porous and covered with moisture	In air	Strongly corrodes and disintegrates into a dark powder
2	Under a slag of $\text{CaCl}_2 + \text{NaCl}$ . Double crystallization. Overheating 20-30°. Chilled. Alloy was dense.	In air	Corrodes slightly
3	Under a slag of $\text{CaCl}_2 + \text{NaCl}$ . Conditions as in Exp. No. 1.	In a desiccator with a flow of dry air	Does not corrode
4	Under a slag of $\text{CaCl}_2 + \text{NaCl}$ . Conditions as in Exp. No. 2.	In a desiccator with a flow of dry air	Does not corrode
5	Under a slag of $\text{BaCl}_2 + \text{NaCl}$ . Conditions as in Exp. No. 1	In air	Does not corrode
6	Smelted in an atmosphere of illuminating gas	In air	Does not corrode.

#### "Spontaneous" Disintegration of Mg - Pb Alloys

For the investigation Mg - Pb alloys were prepared of different concentrations under a slag of  $\text{MgCl}_2 + \text{KCl}$  and in open vessels which were weighed periodically. The alloys were corroded in the usual room atmosphere with small variations of temperature and atmospheric moisture.

The experimental data are presented on the curves in Figs. 1 and 2. The method of presentation and the symbols of the curves are evident from the diagrams.

Alloys No. 1 (70% Mg), No. 2 (40% Mg) and No. 8 (2% Mg) are not presented on Fig. 1, in view of the relatively slight weight increase with the passage of time. The lines "relative gain in weight - time" almost coincide with the abscissa for all these alloys, as is evident from the following data:

Alloys after 120 hours	Relative weight increase after 360 hours
No. 1 .....0.0009	0.0015
No. 2 .....0.0008	0.0008
No. 8 .....0.0005	0.0009

Curve 9 of Fig. 1 presents experimental data of a special experiment, which will be described below.

The curves of Fig. 1 indicate the maximum rate of corrosion for the intermetallic compound  $Mg_2Pb$  (Curve 5) and the least corrosion with increase (Curves 3 and 4) and with decrease (Curves 6 and 7) of the magnesium content.

Analysis of these curves makes it possible to establish the chemism of the "spontaneous" disintegration of the intermetallic compound  $Mg_2Pb$ .

If an increased ratio of metals to oxygen is assumed in the intermetallic compound and that the reaction proceeds according to the equation:



then in this case, after the complete disintegration of the alloy, the relative weight increase should be equal to 0.188. From Fig. 1 it is evident that actually this is not so, since the relative weight increase for the alloy (Curve 5) is considerably higher than this figure. Curve 5 also does not have any significant feature within the given values of the coordinates.

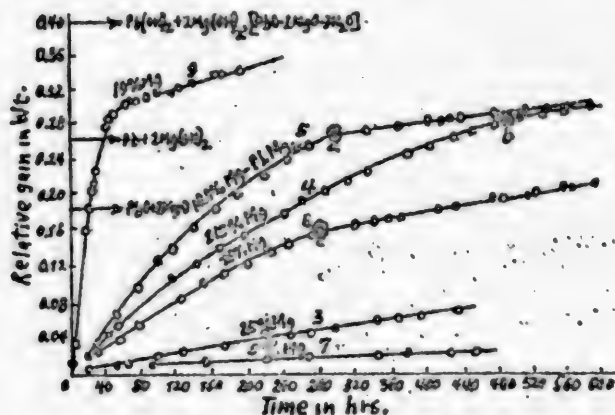


Fig. 1. Disintegration of the Intermetallic Compounds  $Ag_3Al$  and  $Mg_2Pb$

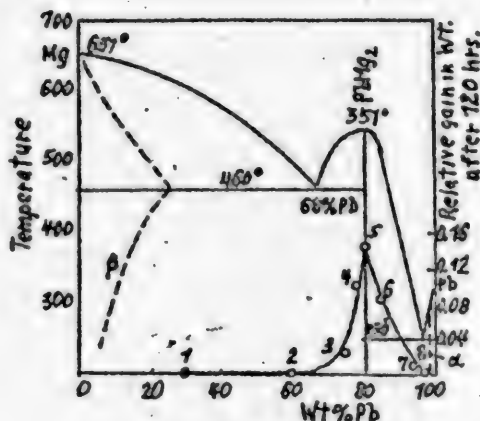
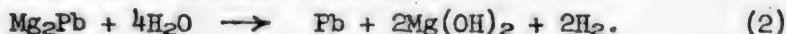


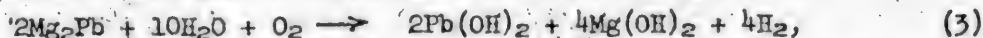
Fig. 2. Disintegration of the Intermetallic Compounds  $Ag_3Al$  and  $Mg_2Pb$

If we proceed from the established experimental fact of the reaction of  $Mg_2Pb$  with water vapor and liquid water, the separation of hydrogen, and from the fact that the initial product of the disintegration is a black powder, then it is possible to postulate the following reaction:



In this case the relative weight increase will be equal to 0.266. In Curve 5 we see the breaking point (a) approximately corresponding to this figure. Above this point a linear increase in weight of the disintegrated alloy takes place because of the oxidation of the slightly dispersed lead and the hygroscopicity of the oxides and hydroxides obtained.

If it is assumed that the chemism of the disintegration of the inter-metallic compound takes place according to the overall equation:



by which the relative weight increase should be 0.399, then in every case in the first phase of the process, this equation is also not realized, since Curve 5 far from approaches this figure.

By the comparison of the given reaction with Fig. 1 (Curve 5) it is very evident that the "spontaneous" disintegration of the intermetallic compound  $\text{Mg}_2\text{Pb}$  in air takes place in the following fashion: first,  $\text{Mg}_2\text{Pb}$  reacts with the atmospheric moisture according to the second reaction, the hydrogen evolved prevents the oxidation of the slightly dispersed lead; at the end of this process there takes place a slow oxidation of the slightly dispersed lead obtained as a product of the reaction (on Curve 5 above point a) and a saturation of the products of corrosion by moisture. The light-yellow corrosion product  $\text{PbO} \cdot 2\text{MgO} \cdot 3\text{H}_2\text{O}$ , established by G. Grube [1,5] is the final product of the series of reactions.

The same may take place for alloys deviating from the stoichiometric composition.

It follows from the phase diagram (Fig. 2) that for an alloy with 15% Mg (excess lead), the excess phase  $\text{Mg}_2\text{Pb}$  will be 0.75 parts in which there will be  $0.75 \times 0.19$  weight parts of Mg. The gain in weight for this quantity by reaction (2) is 0.199. Curve 6 does not reach this quantity. The breaking point (c) corresponds to a weight increase of 0.16. This is explained by the fact that accurate quantitative results as well as accurate quantitative reproducibility could not be obtained in experiments on the investigated corrosion. But the following theoretical consideration is possible. The complete corrosive decomposition in this case may inhibit the eutectic  $\alpha$ -phase (Pb with 0.85% Mg) [7], which is up to 8/9 parts in the eutectic.

Another picture is obtained with the Alloy No. 4 (21.7% Mg). This alloy consists of the initial  $\text{Mg}_2\text{Pb}$  and the eutectic  $\text{Mg}_2\text{Pb} + \beta$  ( $\beta$  = Mg with 25% Pb) [7]. The content of  $\beta$  in the eutectic is in all 13/56 parts, since this stable phase cannot carry out a protective action on the decomposition even of the  $\text{Mg}_2\text{Pb}$  eutectic. In all, the initial and the eutectic  $\text{Mg}_2\text{Pb}$  content in this alloy is 53.3/56 parts. For this quantity the relative gain in weight after the disintegration according to reaction (2) is 0.253. On Curve 4 the breaking point (b) corresponds to 0.280. This increase may be explained by the insignificance of the secondary reactions in these quantitative calculations, which may take place simultaneously with the basic reaction. This factor was in evidence to a great degree in alloy No. 4, since this alloy corroded after a large interval of time. The completion of the first phase of the reaction in alloys No. 6 and 5 took about 12 days, while for alloy No. 4 this reaction was completed only after 20 days.

To test the above postulate, experiment No. 9 was carried out with an alloy with 19% Mg. This alloy was treated under conditions different from that of the other corrosion tests, that is the alloy was kept in an open desiccator over water. "Spontaneous" disintegration took place with great speed (Fig. 1, Curve 9); then, having reached the relative gain in weight corresponding to reaction (2), the curve sharply shifts in direction and almost linearly approaches the figure for the relative gain in weight corresponding to the overall reaction (3), which also corresponds to the final corrosion product  $\text{PbO} \cdot 2\text{MgO} \cdot 3\text{H}_2\text{O}$ , established by Grube [1,5].



In the series of compounds  $\text{Mg}_2\text{Si} \rightarrow \text{Mg}_2\text{Ge} \rightarrow \text{Mg}_2\text{Sn} \rightarrow \text{Mg}_2\text{Pb}$  with an increase of the metallic properties of the elements of the fourth group, the activity of the compounds increases upon reaction with water. Thus,  $\text{Mg}_2\text{Pb}$  actively displaces hydrogen.  $\text{Mg}_2\text{Sn}$  to a lesser degree, and  $\text{Mg}_2\text{Si}$  only undergoes hydrolysis. This agrees well with the probable nature of the chemical bond for these compounds. According to the work of N.V. Areev [8], a superposition of the ionic bond upon the metallic takes place in the crystalline lattice of these compounds. The given elements of the fourth group tend towards anion formation. The strength of the ionic bond, upon shifting to this row, decreases to lead, the electronic affinity drops and the compound more actively reacts with water. The elements of the fourth group in this reaction act as electron carriers from Mg to the hydrogen ion. It is thus clear that the best carrier of this type is lead.

The "spontaneous" disintegration of the intermetallic phases may be utilized as a property in physico-chemical analysis. If in our case, for example, we take the relative gain in weight after 120 hours and place it on the curve as a function of the composition (Fig. 2), then we obtain a curve with a maximum characteristic of the intermetallic compound. This curve also shows the concentration limits for the "spontaneous" disintegration of the Mg - Pb alloys. They correspond to the region of the initial crystallization of  $\text{Mg}_2\text{Pb}$  (3% and 32% Mg).

The investigation of the "spontaneous" chemical disintegration of the metallic phases in air and the establishment of the concentration limits of this process according to the phase diagram will make it possible, in laboratory-industrial practice, to do preliminary work in the choice of the composition of the base-alloy.

The case of the disintegration of the  $\gamma$ -phase Ag - Al indicates the possibility of obtaining a stable intermetallic phase upon using an anhygroscopic slag and by employing a definite system of smelting and casting.

#### SUMMARY

1. The chemical reactions of intermetallic phases were investigated, where the metallic alloys crumble into a powder in air and under usual conditions.
2. It was established that the melting of the compound  $\text{Ag}_5\text{Al}_3$  under a hygroscopic slag does not comply with the postulation expressed by Tamman on the relationship of the chemical activity of metallic compounds to the relative position of the components in the electromotive series. The influence of the nature of the slag used upon the stability of the  $\gamma$ -phase Ag - Al, the temperature of overheating and the double crystallization upon preparation of the alloy were investigated.
3. The kinetics of the reaction of  $\text{Mg}_2\text{Pb}$  with the water vapor of the air were studied. A curve for "corrosion rate - time" was constructed, by which the presence of two reaction phases was established. From the curve "corrosion rate - time" concentration limits were established for the increased corrosive instability of Mg - Pb alloys.
4. The course of the chemical reaction of  $\text{Mg}_2\text{Pb}$  with water was given, which agrees well with the ion-metallic bond in phases of the  $\text{Mg}_2\text{Sn}$  type.

In conclusion, we must express our gratitude to B. G. Pietrenko for his advice in this work.

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# PHYSICO-CHEMICAL INVESTIGATION OF THE SYSTEM SILVER NITRATE-THALLIUM NITRATE IN THE MOLTEN STATE

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The purpose of our work was to investigate the reactions in the system silver nitrate - thallium nitrate in the molten state in order to establish a relationship between the composition and such measurable quantities as electrical conductivity, viscosity and specific gravity. This system is characterized by the fact that the melting point curve, studied by van Wijk, contains a compound at the maximum melting-point temperature corresponding to a ratio of 1:1 of the components and to the formula:  $\text{AgNO}_3 \cdot \text{TlNO}_3$ .

The melting-point data for this system were taken from the handbook of physico-chemical-technical values, "Technical Encyclopedia" [1].

The components of the system are easily fused. This makes it possible to carry out the investigation under comparatively simple conditions. The establishing of certain rules for these simple subjects permits its extension to more difficult subjects and although experimental, has great practical application.

Experimental study of organic and metallic systems shows that best results are obtained by using a series of methods. In this regard it is interesting to observe the position of certain points corresponding to the same composition, upon shifting from the isotherm of one property to the isotherm of another property.

## Specific Gravity

Very few investigators have studied the specific gravities of binary salts found in the molten state. We note the works of A.G. Bergman and Y.I. Schwarzman [2], Korpachiev and Stromberg [3], V.D. Poliakov [4] and others. Their investigations as well as a series of others indicated that the specific gravity of salts in the molten state has a linear relationship to the temperature. Almost all salts, as well as mixtures of salts, conform quite well to the formula:

$$d_t = d_{\text{molten}} - a(t - t_{\text{molten}})$$

The isothermal specific gravity curves on the composition - property diagram have an almost linear character, do not exhibit special points and do not give any indication of the chemistry of salts in the molten state.

Two methods may be used for measuring the specific gravity - the hydrostatic weighing method and the dilatometric method.

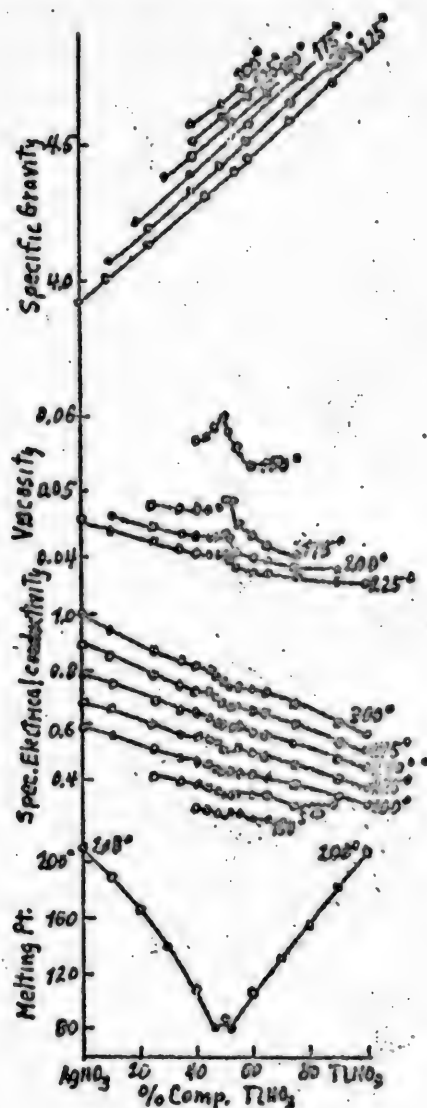
We conducted the specific gravity determinations using a More-Westphal balance with platinum pans submerged in the mixture of molten salts.

In all, eleven compositions were studied. Each composition was studied



at various temperatures. The figures for the determination of specific gravity in the system silver nitrate - thallium nitrate are given in Table 1. On the basis of these figures specific gravity isotherms were constructed which are given on the diagram.

The isothermal specific gravity curves vary almost linearly and do not indicate the chemism.



Phase diagram and curves for the isotherms of the specific electrical conductivity, viscosity, and specific weight of silver nitrate - thallium nitrate in the molten state.

### Electrical Conductivity

At the present time there is extensive material available on the electrical conductivity of individual salts in the molten state. At first it was shown that the electrical conductivity of molten salts varied linearly or almost linearly with temperature. However, more accurate investigations showed that the electrical conductivity did not increase linearly with change in temperature.

The electrical conductivity of molten salts as a function of temperature is expressed as an exponential series of the second or even third power;

$$X = X_0 + C(t - t_0) + D(t - t_0)^2.$$

Very little study has been made of the electrical conductivity of binary salts in the molten state. Without going into further detail on this question we note only the works of Bogorodski, Fusera and Sandonini and others. A detailed survey of these works is given by P.F. Antipin, V.P. Barzakovski, et al [5].

The works of the above authors relate to the first experiments on the application of electrical conductivity as a method of physico-chemical analysis.

These investigations show that the electrical conductivity of molten salts, not forming definite compounds according to the temperature - composition diagram, are the average values for the electrical conductivity of the pure components. However, small deviations from the linearity take place where the magnitude of the electrical conductivity is decreased.

The electrical conductivity isotherms for the system: potassium chloride - calcium chloride and potassium chloride - cadmium chloride, constructed from the

data of Sandonini, indicate a rather deep minimum, which compels us to believe as a result of our investigations, that this minimum electrical conductivity is connected with the presence of a compound in the melt corresponding to the diagrammatic composition. The electrical conductivity isotherms for the system potassium chloride - magnesium chloride, studied by Korpachiev and

Table 1  
Specific Gravity of the System Silver Nitrate - Thallium Nitrate

Composition (wt %)		Specific gravity at the temperatures					
AgNO <sub>3</sub>	TlNO <sub>3</sub>	225°	200°	175°	150°	125°	100°
100	—	3.922	—	—	—	—	—
90	10	4.024	4.074	—	—	—	—
75	25	4.132	4.183	4.245	—	—	—
60	40	4.261	4.319	4.384	4.435	4.502	4.554
55	45	4.304	4.369	4.421	4.485	4.535	4.591
50	50	4.351	4.410	4.475	4.526	4.581	4.630
48	52	4.365	4.421	4.487	4.541	4.597	4.640
45	55	4.406	4.452	4.498	4.575	4.625	4.671
35	65	4.483	4.506	4.612	—	—	—
25	75	4.579	4.638	—	—	—	—
10	90	4.725	—	—	—	—	—

Stromberg [8], also varied quite strongly. The isotherms at first dropped sharply from the potassium chloride ordinate, then in the middle portion of the diagram had a horizontal position, which, beginning with 80% magnesium chloride, again dropped sharply to the ordinate of the pure component, magnesium chloride.

At the present time, on the basis of the mechanisms we established in the field of electrical conductivity of molten salts we may tentatively infer the presence of one or possibly two minima from their experimental data, corresponding to definite compounds at the ordinates of the melting point diagram.

Very extensive research on the application of electrical conductivity as a method of physico-chemical analysis was conducted by A. G. Bergman [2] with the participation of numerous coworkers; these researches led to a series of interesting conclusions.

We studied the electrical conductivity of the system silver nitrate - thallium nitrate in test tubes of refractory glass. As an electrode we used a somewhat modified version of the electrode of Biltz and Klem.

A vacuum tube oscillator with a tuning-fork stabilized oscillation and a vacuum tube amplifier served as a source of high-frequency current in the present work. A detailed description of this apparatus is given in the work of A.G.Bergman [7] and V.D.Poliakov [4].

The electrode was submerged in the test tube with the molten mixture, which was placed in an electric furnace. Regulation of temperature in the electrode furnace was accomplished by means of a rheostat. The temperature was measured with a nichrome-constantan thermocouple, lowered directly into the molten salts. The capacity of the vessel was determined by means of potassium nitrate in the molten state. The data on the specific electrical conductivity for this salt was taken from Landholt's handbook. For the

investigation of the specific electrical conductivity of the system silver nitrate - thallium nitrate, 15 compositions were taken. Each composition was studied at different temperatures. The lowest limit was defined by the appearance of a solid phase, and the highest - by the beginning of decomposition of the nitrates, i.e., at a temperature of 300°. From these polytherms, constructed for mixtures of various compositions, isothermal points at varying specific electrical conductivities were chosen, by which isotherms were constructed.

The figures on the determination of the specific electrical conductivity are given in Table 2. The isotherms of the specific electrical conductivity are shown on Fig. 1.

Table 2

Specific Electrical Conductivity of the System Silver Nitrate - Thallium Nitrate

Composition (in wt. %)		Specific electrical conductivities at the temperatures:								
AgNO <sub>3</sub>	TlNO <sub>3</sub>	300°	275°	250°	225°	200°	175°	150°	125°	100°
100	—	0.993	0.895	0.790	0.691	0.588	—	—	—	—
90	10	0.943	0.849	0.752	0.659	0.560	—	—	—	—
75	25	0.870	0.773	0.686	0.594	0.508	0.417	—	—	—
65	35	0.824	0.743	0.652	0.565	0.480	0.394	—	—	—
60	40	0.808	0.725	0.640	0.555	0.468	0.385	0.295	0.223	0.145
55	45	0.796	0.716	0.619	0.542	0.459	0.371	0.286	0.208	0.135
52	48	0.775	0.695	0.607	0.536	0.440	0.357	0.279	0.195	0.125
50	50	0.753	0.677	0.594	0.511	0.427	0.352	0.270	0.188	0.123
48	52	0.736	0.664	0.586	0.505	0.424	0.349	0.274	0.191	0.127
45	55	0.735	0.661	0.585	0.511	0.424	0.351	0.275	0.208	0.137
40	60	0.722	0.647	0.570	0.494	0.412	0.343	0.259	0.180	0.122
35	65	0.712	0.635	0.561	0.487	0.405	0.336	0.258	0.181	—
25	75	0.676	0.602	0.530	0.458	0.382	0.310	—	—	—
10	90	0.607	0.545	0.476	0.404	0.336	—	—	—	—
	100	0.559	0.500	0.438	0.379	0.318	—	—	—	—

The variation of the specific electrical conductivity of mixtures of salts with temperature, like the pure components in the molten state, has an almost linear character, with the exception of those portions close to the melting points of these salts.

The isothermal curves of the specific electrical conductivity for this system, as plotted on the composition - property diagram, do not have additive properties. They have a general convexity towards the composition axis. Also, the specific electrical conductivity is distinguished by a rather sharp minimum on these isothermal curves. This minimum corresponds to the compound which was found on the melting-point diagram. With increase in temperature a diffusion of this minimum takes place, which evidently indicates a partial dissociation of the above chemical compound found in the molten state.

It is of interest to note that analogous types of isothermal curves were obtained by academicians N.S. Kurnakov, N. A. Trifanov, N. K. Voskresenskaya, S. I. Chierbov, et al [8], for systems with organic substances. This circumstance makes it possible to postulate a somewhat analogous mechanism of electrical conductivity in both cases.

Our conclusions on the relatively similar nature of the chemisms of the

specific electrical conductivity isothermal curves are confirmed by the subsequent works of a group of coworkers, conducted under the general supervision of A.G.Bergman [2].

We calculated the temperature coefficient according to the formula:

$$\alpha = \frac{X_1 - X_2}{(t_1 - t_2)X_{\text{comp.}}},$$

where  $X_1$  and  $X_2$  = values for the specific electrical conductivity for our case at 300 and 250°;

$t_1 - t_2 = 50^\circ$ ;  $X_{\text{comp.}}$  = the value for the specific electrical conductivity at 300°.

The temperature coefficient of the specific electrical conductivity shows a maximum which corresponds to the ordinates of the compound found between silver nitrate and thallium nitrate.

### Viscosity

Thanks to the works of N.S.Kurnakov [8], who investigated a large number of binary organic systems, it was established that the viscosity very definitely corresponds to the action taking place upon mixing of the two components. For systems with distinct chemical reactions there is obtained a sharp, single maximum corresponding to the composition of the compound formed. As an example of such types of diagrams characterized by the formation of chemical compounds, and having specific points on the viscosity isotherm curves, there are the systems: allyl mustard oil - methylaniline; phenyl mustard oil - diethylamine; ethyl formate - tin tetrachloride. From the point of view of physico-chemical analysis, the investigation of the viscosity of binary systems in the molten state is of considerable interest.

Disregarding investigations on borate and silicate systems, we note that the literature on this question is very meagre. As is indicated in the works of V.D. Poliakov [4] and V.P. Barzakovski [10], in systems not containing definite compounds on the melting-point diagram, the viscosity isotherms of binary mixtures of molten salts deviate slightly from linear additiveness for the smaller values of viscosity.

In the case of a system characterized by definite compounds on the melting-point diagram, the viscosity isotherms of binary mixtures of molten salts, as shown by the investigations of A.G.Bergman and U. I. Shwarzman [2] and Korpachieva and Stromberg [6], have a maximum corresponding to the definite compound.

We conducted the determination of viscosity in the system silver nitrate - thallium nitrate with the aid of an Ostwald viscosimeter. To reach the high temperature of the molten salt the viscosimeter was submerged in a furnace-thermostat. To observe more carefully the course of melting in the capillary and to calculate the flow time of the molten mixture, small glass windows were constructed on both sides of the furnace - thermostat, through which was passed light from a 12 volt bulb.

The determination of the temperature was made with a nichrome-constantan thermocouple. The viscosimeter was graduated according to  $\alpha$ -naphthol. The viscosity was calculated from the formula:

$$\eta = \eta_0 \frac{d \cdot t}{d_0 \cdot t_0},$$

where  $\eta_0$  = the viscosity of  $\alpha$ -naphthol at the investigated temperatures,



d and t = the specific gravity and the rate of flow of the investigated mixture,  $d_0$  and  $t_0$ , the same values for  $\alpha$ -naphthol.

For investigating the viscosity of the system silver nitrate - thallium nitrate, thirty compositions were taken, besides the pure components.

The lower limit was defined by the appearance of a solid phase, and the top limit by a temperature of 225°. The values obtained for the viscosity are listed in Table 3.

Table 3

Viscosity of the System Silver Nitrate - Thallium Nitrate

Composition (in wt %)		Viscosity at the temperatures				
AgNO <sub>3</sub>	TlNO <sub>3</sub>	225°	200°	175°	150°	125°
100	—	0.0456	—	—	—	—
90	10	0.0439	0.0461	—	—	—
75	25	0.0424	0.0446	0.0476	—	—
65	35	0.0416	0.0434	0.0473	—	—
60	40	0.0407	0.0432	0.0472	0.0568	0.0740
55	45	0.0404	0.0430	0.0471	0.0572	0.0744
52	48	0.0404	0.0430	0.0469	0.0586	0.0752
50	50	0.0403	0.0433	0.0480	0.0608	0.0776
48	52	0.0398	0.0430	0.0480	0.0580	0.0740
45	55	0.0387	0.0408	0.0446	0.0560	0.0713
40	60	0.0381	0.0400	0.0427	0.0536	0.0700
35	65	0.0378	0.0392	0.0416	—	—
25	75	0.0373	0.0388	0.0407	—	—
10	90	0.0365	0.0383	—	—	—
	100	0.0367	—	—	—	—

The viscosity isotherms are shown on the composition - property diagram (see diagram). The isotherms are drawn at 25° intervals.

The viscosity isotherms shown on the composition - property diagram contain a maximum. This maximum, when referred to the ordinate, corresponds to the relative composition of 1:1, which is the compound found from the melting-point diagram. The closer we approach the crystallization temperature, the sharper this maximum becomes and the more significant is its reflection of the chemism in the given system.

The higher the temperature of the molten mixture, the more pronounced is the diffusion of this maximum on the viscosity isotherm curves. The diffusion of the maxima on the viscosity isotherm curves indicates a partial dissociation of the chemical compound formed in the melt. On the viscosity isotherm curves are also noticed a movement of this maximum towards the same direction which was observed for the movement of the minimum in the isotherm curves for the specific electrical conductivity, *i.e.*, in the direction of thallium nitrate.

#### SUMMARY

1. The system silver nitrate - thallium nitrate in the molten state was investigated in relation to specific gravity, electrical conductivity, and viscosity.

2. The specific gravity isotherms do not show any points corresponding to a definite compound.

3. The specific electrical conductivity isotherms are characterized by a sharp minimum corresponding to a definite compound. With increase in temperature this minimum shifts in the direction of the component with least values for its properties.

4. The viscosity isotherms are characterized by a maximum, corresponding at the ordinate to a definite compound. With increases in temperatures this maximum shifts in the direction of the component with least values for its properties.

5. The maxima on the viscosity isotherms and the minima on the specific electrical conductivity isotherms level off with increase in temperature, which indicates an increase in the dissociation of the compound in the molten state with increase in temperature.

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## PHYSICO-CHEMICAL STUDY OF IODINE SOLUTIONS

### IV. SYSTEMS OF PHOSPHORUS HALIDE-IODINE

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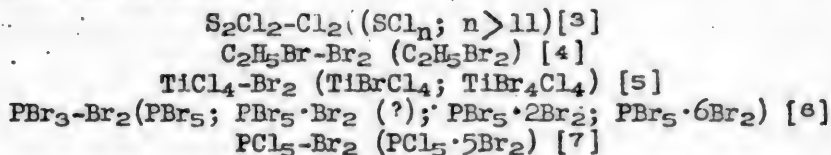
An examination of the properties of polyhalides demonstrates the expediency of differentiating those complex compounds of this type, which are products of the combination of highly polar halides with halogens, from those polyhalides which are formed from nonpolar or slightly polar halides [1].

Almost all the more or less well-studied polyhalides belong to the first of these groups, for example, those which contain the iodides of alkali metals or the iodides of quadruply-substituted ammonium bases etc.

To this same group belong the most characteristic features of the polyhalides, which as complex compounds, express in the mechanism of their formation the nature of the coordination bond, stability, electrochemical properties, and several other properties of these substances.

The second group of polyhalides has received considerably less study. This is explained principally by the fact that in investigations using the thermal method of analysis, the formation of complex compounds could not be detected in a large number of systems\* consisting of halogens and nonpolar or slightly polar halides [2].

The formation of compounds of the polyhalide type has been shown by the method of thermal analysis to exist only in the following systems, one of the components of which is a nonpolar or slightly polar halide (the form in which this compound appears in the given system is shown in parentheses):



Besides these experimental data, obtained by the use of thermal analysis, information is also found in the literature on the production of several so-called higher halides based principally upon work of a preparatory nature. These data are concerned almost exclusively with the halides of phosphorus; they will be brought up later.

In the investigation of compounds of the polyhalide type, as in the investigation of complex compounds in general, a study of their electrochemical properties is of great value. However, the polyhalides formed by nonpolar

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\*Over twenty-five systems of the compositions chlorine-chlorides, bromine-chlorides, iodine-chlorides, bromine-bromides, iodine-iodides.



or slightly polar halides have been subjected to very little study in regard to their electrochemical properties. This question has been studied only in isolated investigations, in which it was shown that several of the systems which were solutions of nonpolar or slightly polar halides in bromine or iodine were distinguished by a considerable degree of electrical conductivity, approaching the electrical conductivity of aqueous solutions of strong electrolytes. These were bromine solutions of phosphorus pentachloride investigated by V.A. Plotnikov and S.I. Yakobson [8], and bromine solutions of phosphorus pentabromide investigated by V.A. Plotnikov [9].

The high electrical conductivity of the bromine solutions of  $\text{PCl}_5$  and  $\text{PBr}_5$  may be explained by the formation of complex compounds in these solutions possessing the character of electrolytes.

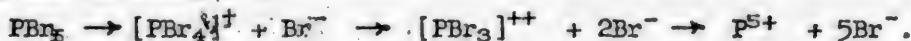
The formation of complex compounds in the system  $\text{PBr}_3 - \text{Br}_2$  was discovered by Biltz and Jepp [6] (see above).

The presence of the polybromide  $\text{PCl}_5 \cdot 5\text{Br}_2$  in the system  $\text{PCl}_5 - \text{Br}_2$  was shown by Plotnikov and Yakobson in the investigation of the melting point curves, in which a dystectic at 22%  $\text{PCl}_5$  was found (theoretically the compound  $\text{PCl}_5 \cdot 5\text{Br}_2$  contains 20.6%  $\text{PCl}_5$ ). A compound of  $\text{PCl}_5$  with bromine was also separated by these authors from a solution in carbon bisulfide. Experiments on the electrolysis of the system  $\text{PCl}_5 - \text{Br}_2$  [7] and  $\text{PBr}_5 - \text{Br}_2$  [9] indicated that chlorine or bromine are separated at the anode approximately in accordance with Faraday's law. In the system  $\text{PCl}_5 - \text{Br}_2$ , chlorine together with bromine was found to separate on the silver anode, which was explained by a secondary reaction - the electrolysis of  $\text{PBr}_5$  formed by the action of phosphorus with bromine, in which according to the opinion of Plotnikov and Yakobson, the former was formed by separation at the cathode.

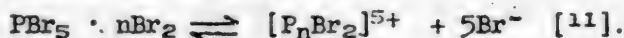
According to the supposition of these authors, the complex  $\text{PCl}_5 \cdot 5\text{Br}_2$  may be expressed by the formula  $\text{P}(\text{ClBr}_2)_5$ .

The following schemes of electrolytic dissociation (applied to  $\text{PBr}_5$ ) are presented in the literature concerning the question of the nature of the ions in bromine solutions of phosphorus pentahalides:

1. According to Walden, who studied the electrical conductivity of  $\text{PBr}_5$  in liquid  $\text{SO}_2$  and in  $\text{AlCl}_3$  [10]:



2. According to V.A. Plotnikov, in bromine solutions of  $\text{PBr}_5$  it is necessary to consider the phenomenon of solvation:



This scheme of electrolytic dissociation agrees with experimental results on the transfer of ions in bromine solutions of  $\text{PBr}_5$  in which it was shown that phosphorus travels to the cathode [12].

In bromine solutions of  $\text{PCl}_5$  and  $\text{PBr}_5$  there is a well-defined connection between the electrochemical properties of these solutions and the formation of complex compounds, in the given case of the higher phosphorus halides.

However the system  $\text{TiCl}_4 - \text{Br}_2$ , in which the formation of two compounds  $\text{TiBrCl}_4$  and  $\text{TiBr}_4\text{Cl}_4$  was found [5], does not carry a current, as was shown by Y.A. Fialkov and I.L. Abarbarchuk [1].

In an investigation of bromine solutions of several halides there also appeared a connection between the electrical conductivity

of these solutions and the association of the corresponding halides [13]. Thus,  $\text{AsBr}_3$ ,  $\text{S}_2\text{Br}_2$ ,  $\text{CCl}_4$ , the molecules of which are monomeric in bromine, form solutions with bromine which do not carry the electric current.\* Bromine solutions of  $\text{SbCl}_3$  [14] and  $\text{SbBr}_3$  possess opposite properties (relative to the concentrations of the solutions [15]).

Analogous properties are also evident with solutions of many iodides in molten iodine: the iodides of mercury, tin, antimony, phosphorus, having a normal molecular weight in iodine solutions, show very little influence on the electrical conductivity of molten iodine, in contradistinction to the iodides of the alkali metals and thallium, which are strongly associated in iodine and form with it systems of high current conductivity [16].

The works mentioned here probably almost completely exhaust the electrochemical investigations described in the literature of bromine and iodine solutions of nonpolar and slightly polar halides. The experimental data obtained in these investigations are insufficient to characterize, electrochemically, the complex compounds formed by such halides with halogens (in particular, with bromine and iodine), in order to clarify the connection between the electrochemical properties of bromine and iodine solutions of such halides and the formation in these solutions of complex compounds of the polyhalide type (or possibly of another type).

The small amount of study devoted to polyhalides formed from nonpolar or slightly polar halides, and the great interest which may devolve upon polyhalides of this type in further characterizing the whole class of compounds related to the polyhalides, prompted us to undertake a study of systems consisting of halides of the above type and halogens.

In the present paper are given results which we obtained in the investigation of solutions of several halides of phosphorus ( $\text{PCl}_3$ ,  $\text{PBr}_3$ ,  $\text{P}_2\text{I}_4$ ,  $\text{PCl}_5$ ) in molten iodine by the methods of thermal analysis and electrical conductivity measurements.

In these systems the formation of higher and also mixed halides of phosphorus could be expected.

In the literature there are reports [17, 18, 19, 20, 21] of the production of a group of compounds similar to the phosphorus halides, which at least by formula may be related to the polyhalides, for example:

- a) Compounds of the type  $\text{PX}_7$ :  $\text{PBr}_7$  [8, 22] or, according to Werner -  $(\text{PBr}_4)(\text{Br}_3)$  [23],  $\text{PCl}_3\text{Br}_4$ ,  $\text{PCl}_2\text{Br}_5$ ,  $\text{PCl}_3\text{I}$  or, according to Baudrimont -  $\text{PCl}_5 \cdot \text{ICl}$  [17], and according to Werner -  $(\text{PCl}_4)(\text{ICl}_2)$  [23];
- b) compounds of the type  $\text{PX}_9$ :  $\text{PCl}_2\text{Br}_7$  [18],  $\text{PBr}_5 \cdot 2\text{Br}_2$  [8];
- c) compounds of the type  $\text{PX}_{11}$ :  $\text{PCl}_3\text{Br}_8$  [18, 19]. According to the literature this compound distills at  $90^\circ$  without decomposition;
- d) compounds of the type  $\text{PX}_{15}$ :  $\text{PCl}_5 \cdot 5\text{Br}_2$  [7] and of the type  $\text{PX}_{17}$ :  $\text{PBr}_5 \cdot 6\text{Br}_2$  [8].

In the systems we investigated - iodine solutions of halides of phosphorus - it was also possible to expect halide exchange reactions and oxidation and reduction reactions.

Thus, according to Baudrimont, phosphorus iodoheptachloride  $\text{PCl}_6\text{I}$  is formed as a result of the following reaction with iodine:




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\* Bromine solutions of aluminum bromide, existing in the form of  $\text{Al}_2\text{Br}_6$ , also does not carry a current. [12]

In citing the data in the literature on the formation of the higher and mixed polyhalides of phosphorus it should be noted that these data refer almost exclusively to works of the 50 - 80s of the 19th century, and were obtained, as previously mentioned, on the basis of work of a preparative nature, with the exception of the investigations described above.

A physico-chemical investigation of systems consisting of phosphorus halides and iodine has not yet been carried out.

## EXPERIMENTAL

### Starting Materials and Method of Investigation

"Chemically pure" preparations of  $\text{PCl}_3$  and  $\text{PBr}_3$  were used. A preparation of  $\text{P}_2\text{I}_4$  with a melting point of  $123.2^\circ$  was used. According to more recent data [24] the m.p. of  $\text{P}_2\text{I}_4$  is  $124.5^\circ$ .

The iodine was distilled 3 times with KI and BaO and once without these substances, then dried in a desiccator over KOH for 3-4 days. The iodine thus purified had a m.p. of  $113.1^\circ$  and an electrical conductivity of  $4.11 \cdot 10^{-5}$  reciprocal ohms. The method of carrying out the thermal analysis and the shape of the vessel which we used have been described in our previous work [25].

For the measurement of electrical conductivity we used the Kohlrausch - Ostwald method. The vessel for measuring the electrical conductivity had platinum electrodes, not platinized. This vessel was submerged in vaseline oil in the thermostat in such a way that the neck of the apparatus up to the stopper was submerged in the liquid; otherwise a sublimation of the iodine on the lower portion of the stopper would take place.

The electrical conductivity of these systems was measured at  $130^\circ$ , and in several experiments also at  $140^\circ$ , in order to determine the value of the temperature coefficient of electrical conductivity. The temperature variation during the experiment did not exceed  $0.3^\circ$ . In order to make absolutely sure that the investigated substances were in solution, the sample was held for some time in the thermostat and the electrical conductivity then determined. The experiment was repeated until duplicating results were obtained.

The electrical conductivity was measured in such a way that at first the iodine was taken and to it the corresponding phosphorus halide was added, and then in a new series of experiments the starting material (solvent) was the phosphorus halide in which the iodine was dissolved and the electrical conductivity determined in this solution.

### Results of the Investigation

#### 1. System $\text{PCl}_3 - \text{I}_2$

Thermal analysis of this system (Table 1) indicated that in adding  $\text{PCl}_3$  to iodine the crystallization temperature gradually drops from  $113^\circ$  to  $102.1^\circ$  at 33 mol% of  $\text{PCl}_3$ , and then remains constant independent of the amount of phosphorus trichloride added, which indicates a limiting solubility of  $\text{PCl}_3$  in iodine, which is located at approximately 33 mol%  $\text{PCl}_3$ .

The data on electrical conductivity obtained for this system (Table 2) is as follows: upon adding  $\text{PCl}_3$  to the iodine (the specific electrical conductivity of which equals  $2.04 \cdot 10^{-5}$  reciprocal ohms), the electrical conductivity at first increases to  $5.6 \cdot 10^{-5}$  reciprocal ohms at 5.16 mol%  $\text{PCl}_3$ , then drops to a value of  $1.3 \cdot 10^{-5}$  reciprocal ohms (at 24.08%  $\text{PCl}_3$ ) and then remains constant.

Table 1  
System  $\text{PCl}_3 - \text{I}_2$

Concentration (in mol %)	Temperature pauses
Iodine .....	113.1
3.8 .....	111.5
12.1 .....	108.4
22.3 .....	104.3
33.0 .....	102.3
37.6 .....	102.1
58.8 .....	102.1

Table 2  
Specific Electrical Conductivity  
of the System  $\text{PCl}_3 - \text{I}_2$  at  $130^\circ$

Concentration of $\text{PCl}_3$ (in mol %)	$\times 10^5$
Iodine .....	2.0
5.2 .....	5.6
8.1 .....	4.3
12.5 .....	2.2
24.1 .....	1.3
29.2 .....	1.2
34.2 .....	1.3

The results of the electrical conductivity measurements for the system  $\text{PCl}_3 - \text{I}_2$  agree with the data obtained in the thermal analysis in the respect that the stabilized values of electrical conductivity and crystallization temperature are located at the same concentration.

#### System $\text{PBr}_3 - \text{I}_2$

Thermal analysis of this system indicated that phosphorus tribromide easily dissolves in iodine, but does not form a compound with the iodine (Table 3 and Fig. 1).\*

Table 3  
Thermal Analysis of the System  $\text{PBr}_3 - \text{I}_2$

Concentration of $\text{PBr}_3$ (in mol %)	Temperature pauses	Concentration of $\text{PBr}_3$ (in mol %)	Temperature pauses
Iodine .....	113.2	67.9 .....	65.4
12.6 .....	103.7	73.3 .....	58.7
21.3 .....	97.2	77.8 .....	52.2
30.0 .....	93.5	81.7 .....	45.0
37.1 .....	88.8	84.6 .....	36.5
45.2 .....	85.5	86.7 .....	30.0
50.0 .....	80.6	88.7 .....	26.0
57.2 .....	74.7	90.8 .....	17.5
63.4 .....	68.4	96.2 .....	- 5.0

The temperature pauses are very sharp. Supercooling did not exceed  $1-2^\circ$ . It should be noted that with increase of the concentration of  $\text{PBr}_3$  there occurs an increase of the formation of the liquid phase, which crystallizes at temperatures below zero. We did not establish these lower temperature pauses.

Upon addition of  $\text{PBr}_3$  to molten iodine, the electrical conductivity of the iodine slowly drops until approximately 19 mol % of  $\text{PBr}_3$  has been added. Upon further increasing the concentration of  $\text{PBr}_3$  the solution does not conduct the electric current.

\* Analogous curves were obtained by Biltz and Meinecke [28] for the systems  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4 - \text{I}_2$ . In all these systems a eutectic was not found, since it was situated very close to the ordinate (the melting point of the corresponding halide.)



In the second series of experiments, the addition of iodine to  $\text{PBr}_3$ , we also could not detect electrical conductivity for this system for contents of  $\text{PBr}_3$  from 94.9 mol.% to 51.5 %  $\text{PBr}_3$ .

### 3. System $\text{P}_2\text{I}_4 - \text{I}_2$

This system was investigated only by the method of thermal analysis. In the work of A.M. Vasil'ev [27] it is shown that  $\text{PI}_3$  with a m.p. of  $61^\circ$  forms a eutectic  $\text{P}_2\text{I}_4$ , with iodine.

Our investigations indicated (Table 4 and Fig. 2), that phosphorus diiodide forms a eutectic with iodine at  $33^\circ$  and 34.3 mol %  $\text{P}_2\text{I}_4$  (probably, close to 33%  $\text{P}_2\text{I}_4$ ).



Fig. 1. Thermal analysis of the system  $\text{PBr}_3 - \text{I}_2$

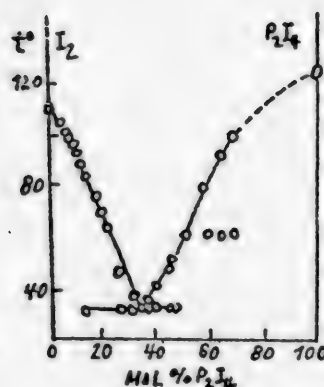


Fig. 2. Thermal analysis of the system  $\text{P}_2\text{I}_4 - \text{I}_2$

Table 4

Thermal Analysis of the System  $\text{P}_2\text{I}_4 - \text{I}_2$

Concentration of $\text{P}_2\text{I}_4$ (in mol %)	Temperature pauses		Concentration $\text{P}_2\text{I}_4$ (in mol %)	Temperature pauses	
	first	second		first	second
Iodine .....	113.3	—	27.1 .....	46.5	33.0
1.1 .....	111.5	—	31.5 .....	38.0	32.8
4.7 .....	104.2	—	34.3 .....	—	33.0
6.4 .....	101.1	—	36.8 .....	36.1	33.0
7.1 .....	99.0	—	39.8 .....	43.0	33.0
8.4 .....	96.0	—	44.5 .....	49.0	33.0
10.2 .....	93.0	—	46.3 .....	52.0	33.0
12.3 .....	87.8	—	50.3 .....	61.0	—
14.3 .....	83.4	32.5	58.5 .....	79.5	61.0
17.7 .....	75.0	—	65.0 .....	91.5	60.2
20.1 .....	69.0	—	67.4 .....	99.0	61.0
21.0 .....	64.5	—			

At 50 mol %  $\text{P}_2\text{I}_4$  the melt has a m.p. of  $61^\circ$  and at this composition, corresponding to  $\text{PI}_3(\text{P}_2\text{I}_4 + \text{I}_2 = 2\text{PI}_3)$ , a concealed maximum is observed on the melting point curve, which is evidenced by the transfer of the eutectic platform from  $33$  to  $61^\circ$ . An investigation of the melting point curve over 68 mol %  $\text{P}_2\text{I}_4$  was not conducted. The formation of  $\text{PI}_5$  and still higher halides was not detected.

### 4. System $\text{PCl}_5 - \text{I}_2$

In a study of this system it was necessary to consider that, according to the data of Baudrimont [17],  $\text{PCl}_5$  reacts chemically with iodine, from which reaction  $\text{PCl}_3$  and  $\text{PCl}_5\text{I}$  (or  $\text{PCl}_5 \cdot \text{ICl}$ ) are obtained.

The formation of these substances may be explained in the following fashion:  $\text{PCl}_5$  is reduced by the iodine to  $\text{PCl}_3$ , the iodine thus formed combines with the excess  $\text{PCl}_5$  to form the complex compound  $\text{PCl}_5 \cdot \text{ICl}$ , which may be

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In the work of Baudrimont [17] it was shown that this substance was also directly obtained by the combination of  $\text{PCl}_5$  with  $\text{ICl}$  or  $\text{PCl}_3$  with  $\text{ICl}_3$  and upon the action of  $\text{PCl}_5$  on  $\text{ICl}_3$ .

represented by the following equations:



As a result the total equation (III) is obtained, as was shown by Baudrimont.

This explanation of the nature of the chemical reaction in the system  $\text{PCl}_5 - \text{I}_2$  required experimental confirmation.

A thermal analysis of the system  $\text{PCl}_5 - \text{I}_2$  was carried out in a concentration interval from zero to almost 80 mol%  $\text{PCl}_5$ . At higher concentrations of  $\text{PCl}_5$  this system could not be investigated because the excess  $\text{PCl}_5$  readily sublimed at the temperature of the experiments (over  $200^\circ$ ). At this temperature  $\text{PCl}_3\text{I}$  also sublimed [17].

The results of the thermal analysis are given in Table 5 and on Fig. 3.

Table 5  
Thermal Analysis of the System  $\text{PCl}_5 - \text{I}_2$

Concentration of $\text{PCl}_5$ (in mol %)	Temperature pauses		Concentration of $\text{PCl}_5$ (in mol %)	Temperature pauses	
	first	second		first	second
Iodine .....	113.2	—	52.2 .....	116.5	—
10.1 .....	105.0	—	52.9 .....	118.2	79.0
18.1 .....	97.5	79.5	53.1 .....	122.0	79.3
28.4 .....	82.0	79.0	57.5 .....	136.0	79.5
31.8 .....	80.5	79.8	65.3 .....	163.0	79.5
33.9 .....	80.2	—	70.0 .....	187.0	—
36.4 .....	90.0	79.5	74.0 .....	198.0	—
39.5 .....	92.1	79.9	76.3 .....	Exact determinations were impossible due to the sublimation of $\text{PCl}_5$ and $\text{PCl}_3\text{I}$ .	
44.5 .....	101.5	79.3	79.7 .....		
47.8 .....	106.5	—	100.0 .....		
50.4 .....	112.5	78.0			

The second as well as the first pauses were very sharp, almost no supercooling having been observed. Upon increasing the concentration of  $\text{PCl}_5$  the amount of liquid phase then formed increased, phosphorus trichloride having been formed.

The formation of  $\text{PCl}_3$ , boiling at  $76-78^\circ$ , complicated the investigation of the system  $\text{PCl}_5 - \text{I}_2$ , and besides, considerably hampered the experimental work, especially in those cases where the melt had a melting point considerably higher than the boiling point of  $\text{PCl}_3$ .

This situation compelled us to change the form of the vessel in which the determination of the crystallization temperature was carried out. For this purpose there was sealed to the vessel a side arm, bent and sealed at the bottom (Fig. 4), in which the  $\text{PCl}_3$  formed by the reaction between  $\text{PCl}_5$  and iodine was condensed.

We used this vessel only for  $\text{PCl}_5$  contents greater than 50 mol %, since with smaller quantities of  $\text{PCl}_5$  a portion of the iodine passed over into the side arm together with the  $\text{PCl}_3$ .

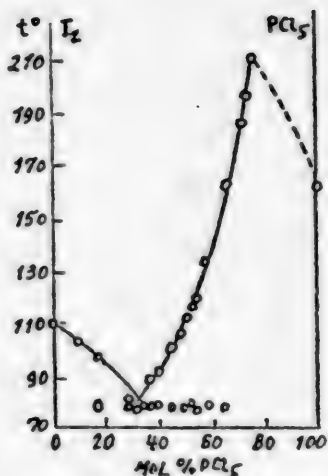


Fig. 3. Thermal analysis of the System  $\text{PCl}_5 - \text{I}_2$



Fig. 4. Vessel for determining the crystallization temperature of the system  $\text{PCl}_5 - \text{I}_2$

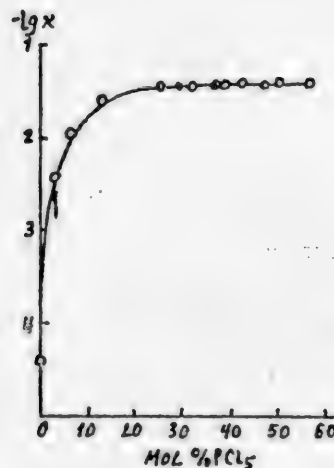


Fig. 5. Specific electrical conductivity of the system  $\text{PCl}_5 - \text{I}_2$  at  $130^\circ$

As is evident from the data of Table 5 and Fig. 3, a eutectic at 33.9 mol %  $\text{PCl}_5$  and  $79.5^\circ$  is observed in the system  $\text{PCl}_5 - \text{I}_2$ . Then upon increasing the  $\text{PCl}_5$  the melting point curve increases up to  $198^\circ$  at 74 mol %  $\text{PCl}_5$ .

The fact that the eutectic pauses ( $79.0 - 79.5^\circ$ ) cease at a  $\text{PCl}_5$  content of about 70 mol % and that the melting point curve should be further lowered to the melting point of the pure  $\text{PCl}_5$  ( $162^\circ$ ) permits the postulation that there should be a maximum on the melting-point diagram corresponding to a region of concentration close to 75 mol %  $\text{PCl}_5$ , *i.e.*, to that ratio of  $\text{PCl}_5$  and iodine which is expressed by the summed equation (III).

In order to prove that the reaction between iodine and  $\text{PCl}_5$  at a  $\text{PCl}_5$  content of about 75 mol % actually proceeds according to the given equation, the following experiment was performed: 11.15 g of  $\text{PCl}_5$  and 4.19 g of iodine (76.43 mol %  $\text{PCl}_5$ ) was placed into the vessel described in Fig. 4, and after melting was heated until the  $\text{PCl}_3$  ceased passing over into the side-arm. After cooling, the side-arm was carefully opened and its contents - a colorless liquid - carefully collected and weighed. 2.23 g of a liquid was obtained which was shown to be  $\text{PCl}_3$ . This was determined by the boiling point of the liquid and by chemical reactions: after decomposition of the liquid by water, the solution obtained gave reactions for phosphorus acid and chloride ion. Theoretically, according to equation (III), 2.27 g of  $\text{PCl}_3$  should have separated figuring on the amount of iodine taken for the reaction, or 2.45 g. if figured on the amount of  $\text{PCl}_5$  taken for the experiment.

After distillation of the  $\text{PCl}_3$  a crystalline substance of an orange-yellow color remained in the vessel, which volatilized upon strong heating, decomposed by the action of water, dissolved in nitrobenzene and was insoluble in  $\text{CCl}_4$  and ethyl bromide.

This substance was subjected to chemical analysis. A sample of the substance was treated with a saturated aqueous solution of sulfur dioxide. In the colorless solution obtained the amount of iodine was determined by titration

At this point a small quantity of the excess  $\text{PCl}_5$  sublimes.



with a solution of  $\text{AgNO}_3$  (indicator, nitroso-starch paper) [28], then an excess of  $\text{AgNO}_3$  was added, titrated according to the Vollhard method, and the amount of chlorine determined.

For the quantitative determination of phosphorus a portion of the solution was oxidized with nitric acid, after which the phosphorus was precipitated as the ammonium salt of phosphomolybdic acid, which was then titrated with a solution of alkali.

#### Results of the Analysis

0.2582 g substance: 6.88 ml 0.1 N  $\text{AgNO}_3$ .

Found %: I 33.81

$\text{PCl}_5\text{I}$ . Calculated %: I 34.28.

0.2582 g substance: 40 ml 0.1 N  $\text{AgNO}_3$ .

Found %: Cl 54.92

$\text{PCl}_5\text{I}$ . Calculated %: Cl 57.37.

0.2852 g substance: 72.16 ml 0.1 N  $\text{NaOH}$

Found %: P 9.41

$\text{PCl}_5\text{I}$ . Calculated %: P 8.36.

The results of the analysis give basis for the belief that the orange-yellow substance remaining after the removal of the  $\text{PCl}_3$  is  $\text{PCl}_5\text{I}$ , evidently contaminated with  $\text{PCl}_3$ .

We obtained a substance of the same color and other similar external characteristics by fusing  $\text{PCl}_5$  and  $\text{ICl}$ , taken in equimolar quantities.

These facts confirm that  $\text{PCl}_5$  and iodine, taken in the ratio of 3 moles of  $\text{PCl}_5$  to 1 mole of iodine, react with each other according to equation (III).

In order to explain the course of reaction between  $\text{PCl}_5$  and iodine at close to equimolecular ratios, the above-described experiment was repeated, taking for the experiment 2.72 g of  $\text{PCl}_5$  and 3.87 g of iodine (46.1 mol%  $\text{PCl}_5$ ).

The liquid distilled into the side-arm was of an orange-crimson color and was shown to be a solution of iodine in phosphorus trichloride. 0.622 g of this substance was collected. After treating the liquid with a solution of  $\text{SO}_2$  its iodine content was determined, which was shown to be equal to 0.046 g; therefore, 0.576 g of  $\text{PCl}_3$  was distilled off. This quantity is very close to the theoretical - 0.597 g  $\text{PCl}_3$ , if we proceed from the weight of  $\text{PCl}_5$  taken and calculate according to equation (III), but on no account from equation (I).

After the distillation of the  $\text{PCl}_3$ , a substance of a dark brown color remained in the vessel, and contained a large quantity of free iodine that had not entered into the reaction. This iodine was separated by dissolving it in  $\text{CCl}_4$ , after which there was left in the vessel a small quantity of an orange-yellow substance, melting in a sealed capillary at  $214^\circ$ , very similar in external appearance to the substance obtained in the first experiment.

Thus it was shown that at a  $\text{PCl}_5$  content considerably less than 75 mol % the reaction does not take place exclusively according to equation (I), but principally according to equation (III), evidently because of the fact that the  $\text{ICl}$  formed immediately combines with the  $\text{PCl}_5$  not yet having entered into the reaction, forming  $\text{PCl}_5\text{I}$ . As a result of this a large quantity of unreacted iodine remains.

The considerably greater rate of reaction of  $\text{PCl}_5$  with  $\text{ICl}$  than with

iodine attests to the relative stability of the complex  $\text{PCl}_5 \cdot \text{ICl}$ .

Arising from the fact that this complex is insoluble in  $\text{CCl}_4$ , we developed the following method for preparing it: solutions of  $\text{PCl}_5$  and iodine in carbon tetrachloride were prepared and mixed in a ratio corresponding to equation (III), i.e., 3 moles of  $\text{PCl}_5$  for 1 mole of iodine; at this point the solution of iodine decolorized and a yellow-colored precipitate separated; this precipitate was filtered through glass wool with the necessary precautions taken against the action of atmospheric moisture upon it; it was washed with  $\text{CCl}_4$  and dried at  $75-80^\circ$ . The substance obtained was of a clear lemon-yellow color, considerably lighter than the product which separated from the system  $\text{PCl}_5 - \text{I}_2$ .

0.2122 g substance: 5.75 ml 0.1N  $\text{AgNO}_3$ .

Found %: I 34.41.

$\text{PCl}_5\text{I}$ . Calculated %: I 34.23.

0.2122 g substance: 34.0 ml 0.1 N  $\text{AgNO}_3$ .

Found %: Cl 57.14.

$\text{PCl}_5\text{I}$ . Calculated %: Cl 57.37.

0.2122 g substance: 54.9 ml 0.1 N  $\text{NaOH}$ .

Found %: P 8.70.

$\text{PCl}_5\text{I}$ . Calculated %: P 8.36.

The substance obtained was very slightly soluble in  $\text{CCl}_4$  and in ethyl bromide; it was soluble in ether, dioxane, chloroform, and nitrobenzene. The solution in dioxane did not carry a current; the specific electrical conductivity of the chloroform solutions was of the order of  $10^{-5}$  mho, and the nitrobenzene solutions of the order of  $10^{-3}$  mho. Water and alcohol ( $96^\circ$ ) decompose this substance; it is also decomposed in moist air. As concerns heating, this complex appeared rather stable, upon heating to  $200^\circ$  it begins to sublime without noticeable decomposition; m.p. (in a sealed capillary)  $212-214^\circ$  with incipient decomposition; upon heating to  $220-222^\circ$  a frothing of the liquid is observed.

The fact that a complex of the composition  $\text{PCl}_5\text{I}$  melts at  $212-214^\circ$  confirms the postulate expressed above that on the melting-point diagram of the system  $\text{PCl}_5 - \text{I}_2$  (from which the  $\text{PCl}_3$  formed was separated), there should be a dystectic corresponding to 75 mol % of  $\text{PCl}_5$ : In this case the ascending branch from the eutectic ( $\sim 34$  mol %  $\text{PCl}_5$ ) on the melting-point diagram would be the curve for the separation of  $\text{PCl}_5\text{I}$ , which also explains its occurrence in the melt of  $\text{PCl}_5$  with iodine at 50 mol %  $\text{PCl}_5$ .

Electrochemical Investigations. These investigations were performed in order to determine the structure of the complex  $\text{PCl}_5\text{I}$ . With this aim the electrical conductivity of the system  $\text{PCl}_5 - \text{I}_2$  was measured and an electrolysis of  $\text{PCl}_5\text{I}$  in a solution of nitrobenzene was conducted. The electrical conductivity of the system  $\text{PCl}_5 - \text{I}_2$  was measured to 60 mol %  $\text{PCl}_5$  (Table 6, Fig. 5).

The specific electrical conductivity isotherm of the system  $\text{PCl}_5 - \text{I}_2$  has an unusual character. At first it rises very sharply upon addition of comparatively small quantities of  $\text{PCl}_5$ . Thus, with a  $\text{PCl}_5$  content of 4.18 mol % the specific electrical conductivity equals  $3.6 \cdot 10^{-3}$  mho, which is 90 times the actual electrical conductivity of molten iodine at  $130^\circ$ . With further addition of  $\text{PCl}_5$  the specific electrical conductivity continues to increase to  $4 \cdot 10^{-2}$  mho - at  $\sim 33$  mol %  $\text{PCl}_5$  it hardly varies any further up to

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Or 50 mol. %  $\text{PCl}_5$  in the system  $\text{PCl}_5\text{-ICl}$ .

~ 60 mol %  $\text{PCl}_5$ . Measurements at higher concentrations were not carried out because of the difficulty of holding the system  $\text{PCl}_5 - \text{I}_2$  in a supercooled condition at these concentrations of  $\text{PCl}_5$ . The electrical conductivity of the system  $\text{PCl}_5 - \text{I}_2$  was measured at  $130^\circ$  and only partially at  $100 - 120^\circ$  and  $140^\circ$  in order to determine the temperature coefficient of electrical conductivity. It is positive in the given system, its value decreasing with concentration of  $\text{PCl}_5$  (Table 7).

Electrical conductivity measurements indicated that the system  $\text{PCl}_5 - \text{I}_2$  possesses a high electrical conductivity, the value of which approximates the electrical conductivity of aqueous solutions of strong electrolytes. As concerns the nature of the electrolyte in the system  $\text{PCl}_5 - \text{I}_2$ , the experiments described above served as a basis for ascribing the electrical conductivity of this system to the electrolytic dissociation of the complex compound of  $\text{PCl}_5$  with iodine chloride -  $\text{PCl}_6\text{I}$ .

In order to explain the nature of the ions into which this complex dissociates, an electrolysis of its solutions in nitrobenzene was conducted. The electrolysis was performed in a U-shaped vessel with a wide glass stopcock in the middle portion of the vessel, permitting a separation of the cathodic and anodic portions of the liquid.

Table 7

Temperature coefficient of Electrical Conductivity of the system  $\text{PCl}_5 - \text{I}_2$

$\text{PCl}_5$ (mol %)	Tempera- ture	Specific Electrical Conductivity in mho $\times 10^2$	Temperature coefficient $100-130^\circ$ $\text{c} \cdot 10^2$
26.3	$100^\circ$	1.8	2.96
	130	3.4	
38.4	100	2.6	1.92
	130	4.1	
50.7	123	3.5	1.0
	130	3.9	
60.9	100	3.0	
	120	3.5	
	130	3.9	
	140	4.2	

Table 6

Specific Electrical Conductivity of the system  $\text{PCl}_5 - \text{I}_2$  at  $130^\circ$

Concentra- tion $\text{PCl}_5$ (mol %)	$\times 10^{-5}$	Concentra- tion $\text{PCl}_5$ (mol %)	$\times 10^{-5}$
Iodine....	4	38.1 ...	4000
4.2 ....	360	38.4 ...	4100
7.4 ....	1110	40.6 ...	4000
14.2 ....	2520	42.9 ...	3900
26.3 ....	3400	48.7 ...	4000
29.0 ....	3600	50.7 ...	3900
32.8 ....	4100	57.0 ...	4000

In a large number of experiments a platinum cathode and a silver anode were used, prepared according to Bruner. In several experiments the cathode was silver and the anode platinum. The solution for electrolysis contained 1.1 %  $\text{PCl}_6\text{I}$ . The color of these solutions was orange-yellow. The electrolysis was conducted at a potential of 40-240 V. The initial current strength -  $8\mu\text{A}$  - was gradually decreased almost to zero. The duration of the electrolysis was 18 - 19 hours.

In the process of electrolysis the liquid at the anode gradually becomes reddish-brown, acquiring the color of solutions of iodine in nitrobenzene. The brown color formation, starting at the anode, gradually extends to the entire anodic liquid and upon prolonged electrolysis passes over to the cathodic portion of the vessel. In contradistinction to this the solution at the cathode gradually lightens and finally acquires the

color characteristic of nitrobenzene, which is accompanied by a discontinuance of the current. An evolution of gas bubbles is noticed at the cathode during the electrolysis.\* The platinum cathode was not changed in the least. The silver anode, however, continually increased in weight. Thus, for example, in one of the experiments the gain in weight at the anode was 0.0177 g.

If the yield is calculated from the current, bearing in mind that only chlorine precipitates at the anode -  $2\text{Cl}$  for 1 F,\*\* then the anode should have only increased by 0.0128 g. Therefore, it may be supposed that iodine precipitates at the anode together with chlorine.

Chemical analysis of the cathodic and anodic liquids showed the following.

The presence of iodine could not be detected in the colorless portion of the cathodic liquid obtained after prolonged electrolysis. In experiments conducted with platinum anodes an increase in the concentration of iodine in the anodic liquid was detected; at the same time an increase in the concentration of phosphorus in the cathodic liquid was observed, as is evident, for example, from Table 8.

The results of these experiments give us a basis for supposing that in the complex compound  $\text{PCl}_3 - \text{ICl}$  the phosphorus and part of the chlorine form a cation of this complex, most probably of the composition  $[\text{PCl}_4]^+$ , the iodine forming an anion with the remaining portion of the chlorine,  $[\text{ICl}_2]^-$ .

Table 8  
Electrolysis of the System  $\text{PCl}_3\text{I} - \text{C}_6\text{H}_5\text{NO}_2$

Substance determined	Solution after electrolysis					
	Anodic Portion			Cathodic Portion		
	should be (g)	Found (g)	$\Delta$	should be (g)	found (g)	$\Delta$
I	0.2558	0.4131	+0.1573	0.2180	0.0634	-0.1546
P	0.0624	0.0581	-0.0043	0.0530	0.0574	+0.0044

#### CONCLUSIONS

We conducted investigations of iodine solutions of the phosphorus halides  $\text{PCl}_3$ ,  $\text{PBr}_3$ ,  $\text{PI}_3$  and  $\text{PCl}_5$  and the results obtained permit the following conclusions to be drawn.

1. The trihalides of phosphorus differ considerably from the pentahalides in their relationship to iodine.

$\text{PCl}_3$  has a limited solubility in iodine. The melting point diagram, investigated in the region of concentration corresponding to the higher halides of phosphorus, did not show the formation of the latter. It must also be noted that, from the data, iodine does not form a compound with  $\text{PCl}_3$ .

The electrical conductivity of the systems  $\text{PCl}_3 - \text{I}_2$  and  $\text{PBr}_3 - \text{I}_2$  is lower than the electrical conductivity of molten iodine.  $\text{PBr}_3$  does not form a compound with iodine.

The diiodide of phosphorus  $\text{P}_2\text{I}_4$  does not form with iodine either  $\text{PI}_5$  or higher polyhalides. The electrical conductivity of this system was not measured, but it may be supposed that it is also comparatively small, as is evident from the results for the electrical conductivity of the system  $\text{PI}_3 - \text{I}_2$  [18].

At this point it is also necessary to bear in mind that beginning with

\* Upon passing the gas bubbles into a solution of  $\text{AgNO}_3$  a turbidity of the solution and a slight precipitate formation were observed.

\*\* As it must follow from our postulated structure of the complex  $(\text{PCl}_4)(\text{ICl}_2)$ .



33 mol%  $P_2I_4$ , the system  $P_2I_4-I_2$  is converted to the system  $PI_3-I_2$ .

2. Iodine solutions of  $PCl_5$  possess quite different properties. In these solutions a high electrical conductivity was found, reaching  $4 \cdot 10^{-2}$  mho and caused by the electrolytic dissociation of the complex  $PCl_6I$ , formed by the action of  $PCl_5$  with iodine. This complex was first obtained and briefly described by Baudrimont. From Baudrimont's work, however, it could not be concluded that the complex  $PCl_6I$  was obtained by him in an isolated condition.

Our investigations confirmed the data of Baudrimont that  $PCl_3$  and  $PCl_6I$  are formed by the action of  $PCl_5$  with iodine, explained how intermediate reactions lead to the formation of  $PCl_6I$  in the system  $PCl_5 - I_2$ , and also presented new methods for obtaining  $PCl_6I$  in an isolated condition from solutions of  $PCl_5$  and iodine in  $CCl_4$ .

The investigations described in this work also confirmed the statements of Baudrimont and Werner that  $PCl_6I$  may be considered as a product of the combination of  $PCl_5$  with iodine chloride.

The structure of  $PCl_6I$  (or  $PCl_5 \cdot ICl$ ) may be expressed by the formula  $[PCl_4]^+[ICl_2]^-$  with a complex cation and anion. A cation of this composition was found in the crystalline lattice of  $PCl_5$ .

Therefore, the complex  $PCl_6I$  must be considered not as a polyhalide as was assumed by Werner; [23], but as a double halide (halide-salt), formed according to the reaction:



As is known from the data in the literature [29], the structure of the  $PCl_5$  molecule in the gaseous and liquid state may be represented by a triangular bipyramid, in which the P-Cl bond at the vertical axis is evidently characterized by a greater space interval than the P-Cl bond at the horizontal plane.

The dipole moment of  $PCl_5$ , measured in solutions of  $CCl_4$  and  $CS_2$ , is in all probability equal to zero.

In the crystalline state phosphorus pentachloride forms a lattice of  $[PCl_4]^+$  cations and  $[PCl_6]^-$  anions, which attests to the polarizability of the  $PCl_5$  molecule. In this respect,  $PCl_5$ , as noted in the literature, may react as  $PCl_3 \cdot Cl_2$ , or as  $[PCl_4]Cl$ .

The results of the investigation of the system  $PCl_5 - I_2$  indicate that  $PCl_5$  reacts with iodine (oxidizes it to  $ICl$ ) as if it had the formula  $PCl_3 \cdot Cl_2$ . Upon reaction with polar (although weakly polar) molecules of  $ICl$ , phosphorus pentachloride polarizes and is converted to  $[PCl_4]Cl$ , after which it combines with the  $ICl$  as a complex.

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## CHEMISTRY OF VISCOSE AND XANTHOGENATES

### III. OXIDATION REACTIONS IN ALKALICELLULOSE AND VISCOSE

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Although cellulose slowly and weakly oxidizes in air (oxygen), it is also capable, however, of being quickly oxidized (autooxidation), as with other hydroxyl-bearing substances, in an alkaline medium such as alkali celluloses or cuprammonium solutions, but in the latter case the oxidative phenomena are also extended to ammonia. Complex phenomena including those of an oxidative nature take place in viscose, especially filtered viscose, its de-aerated product, etc. In viscose, the action of oxygen is directed in large measure to sulfur-bearing substances, including the xanthogenate groups, but is directed least of all towards cellulose.

S. N. Danilov et al, [1], have devoted a series of works to oxidative processes in cuprammonium solutions and to the role of retarders (inhibitors) of oxidation (sodium sulfite, etc.).

Alkalicellulose and cuprammonium solutions of cellulose are media for the oxidative processes due to the oxygen of the atmosphere, since substances such as sulfite participate in the oxidative processes, which evidently have the character of chain reactions.

In cuprammonium solutions there is a powerful carrier of oxygen, i.e., copper ions in tetraamino complexes. In alkali cellulose the alkali activates the oxidative transformations, since the hydrogen atoms in the alcohol groups of cellulose evidently shake loose (become mobile) under the action of alkali. Oxygen, initiating the oxidation reaction, may then split off into an active form, which intensifies the oxidative reactions taking place on the large external and internal surfaces of the cellulose fiber according to a kind of topochemical and catalytic reaction. Increasing the temperature sharply intensifies the oxidative transformations of cellulose, which is well known in the case of the aging (preripening) of alkali cellulose. The oxidation of alkali cellulose serves as an interesting example for the study of the oxidation of cellulose and the inhibitory action of various additives.

Oxidative transformations, as applied to cellulose in alkali cellulose and in cuprammonium solutions, have many general features, if we lay aside the oxidation of ammonia, the question of the role of its oxidation products and the properties of cuprammonium solutions, and also do not consider that the copper complexes are more powerful oxidation accelerators than alkali in alkali cellulose. Oxidative reactions in alkali cellulose and in cuprammonium solutions may be retarded by the addition of several anti-oxidizers (oxidation inhibitors). A series of anti-oxidizers (sulfite, thiosulfate, organic oxy-compounds) were introduced into alkali cellulose and their action in cuprammonium solutions of cellulose were also examined. Oxidants and anti-oxidants

are examined below and are proposed for introduction into alkali cellulose and into viscose.

Transformations in viscose are considerably more varied than in any other known hydrophylic cellulosic colloidal system. In it chemical transformations take place continuously and are brought about by accompanying colloidal-chemical changes, which occur right from the beginning in the preliminary stages of the preparation of viscose (mercerization, aging of alkali cellulose, xanthogenation). Among the various phenomena taking place at different stages of the viscose process, the oxidative processes are of great significance not only at the stage of mercerization of cellulose and its aging, but in viscose itself. Anti-oxidants such as sodium sulfite influence the oxidative processes, beginning with the mercerization of cellulose. However the principal role of the sodium sulfite type of anti-oxidant in viscose is in combination reactions with sulfur, as was shown in our investigations conducted for many years at the Leno Soviet Laboratory of the Leningrad Technological Institute.

Although oxidative processes do not play such a great role in viscose as in the aging of cellulose, oxidative reactions do however take place in viscose and will be examined in this paper.

Of course the primary role in viscose is played firstly by the hydrolytic processes of oxidation - reduction by means of water and alkali, such as: hydrolysis of the trithiocarbonate and the xanthogenates of cellulose; and secondly, by redistribution reactions of sulfur in compounds, accompanied by shifts to higher and lower valence stages, these reactions being especially influenced by the introduction of addition agents which may combine with and separate the sulfur from the polysulfur compounds (potassium cyanide, sulfite and sodium arsenite). However more will be said of these redistribution processes of sulfur in a succeeding paper. At this time we will be concerned with oxidative reactions at various stages of viscose production.

Because of its great practical and theoretical significance, oxidation by atmospheric oxygen has for a long time attracted considerable attention. The action of various catalyzers (oxidants and anti-oxidants), accelerating or on the other hand slowing down or inhibiting oxidation, is of great significance to the theory of the oxidative processes.

In accordance with the well-known theory of Bach-Engler [2], oxidative reactions by the action of oxygen are assumed to take place by the initial formation of peroxides as a result of the combination of two atoms of oxygen by a multiple bond or hydroperoxides as a result of oxygen entering between carbon and hydrogen atoms, the oxygen molecules having been activated by the substratum and shifted into the active form  $-O-O-$  with free valences. In atmospheric oxidation reactions, a large part is played by the affinity of the substance to oxygen, clearly shown for unsaturated substances, carbonyl and oxycarbonyl compounds, etc., and in particular, for cellulose.

Several authors suppose (Haber [3]) that a cleavage of the oxygen molecule to atoms takes place first in the oxidative phenomena, and that otherwise the reaction would evidently take place as with the oxidation of ethylene to ethylene oxide.

Since the cleavage energy of water to hydrogen and hydroxyl is equal to 115 kilo-cal., and the cleavage energy of oxygen to the separate atoms is expressed by the almost similar figure of 117 kilo-cal, there is no need to suppose that oxidation by free oxygen must necessarily take place by the participation of the hydroxyls of water, as was believed by Traube [2]. The activation



of the oxygen molecule  $-O-O-$  should take place more readily by the weakening of one of the two bonds which connect the atoms in the molecule of oxygen; such an activated molecule readily yields the peroxide. Even in the absence of water, oxygen may form peroxides, for example, the peroxide of triphenylmethyl, the hydroperoxide of tetralin, etc., But, however, as concerns the oxidative phenomena in relation to cellulose in cuprammonium solutions, to alkali cellulose and to viscose, the participation of water may be possible since water causes a swelling of cellulose. Therefore, Bach's postulation on the hydrated ions of hydrogen and hydroxyl [2] deserves consideration.

But this postulation is of more interest for the oxidative transformations accompanying the hydration, i.e., the addition of elements to hydrogen peroxide which is observed in the oxidation of ethylene hydrocarbons by potassium permanganate. In the presence of alkali, the hydrogen atoms of cellulose are probably much more mobile than in cellulose swelled in pure water.

Concerning the burning of atomic hydrogen, works of the school of N. N. Semienov have pointed out the role of hydroxyl, the hydrogen peroxide radical  $-HO_2$  and hydrogen peroxide in the formation of chain reactions. The production of the chain reaction may be connected with the appearance of the free hydroxyl, arising from the action of a hydrogen atom in the molecule of the substance with molecular oxygen, at which atomic oxygen forms, producing the oxidation. According to the opinions of various investigators (V. N. Kondratyev [4]), this process may be an initiating one. In the reaction of hydroxyls the formation of atomic oxygen takes place:



Oxidative processes, especially under conditions of rapid reaction rates, may be profitably examined in the light of studies on chain reactions, which would also help explain the action of oxidation inhibitors as agents that interrupt the oxidation chain reaction. However, in explaining the role of the inhibitor, other matters must be considered. It may be postulated that inhibitors, as for example sodium sulfite, protect the most active portions in the cellulose molecule from the action of oxygen, adding to the carbonyl groups and thus retarding the oxidation reaction. But this method of inhibiting oxidation reactions in the presence of anti-oxidants can only be effective with considerable quantities of the anti-oxidant. Not precluded was the possibility of two independent methods, that is a double mechanism of anti-oxidant reaction - by interruption of the chain reaction and by blocking the cellulose groups capable of oxidation. There are definite indications in the literature that oxycellulose combines with sodium sulfite [5].

The presence of various oxidants and principally anti-oxidants may be shown in viscose. Oxidative reactions in viscose are very complex and are evidently distributed primarily among its sulfur-containing components, which are easily oxidized.

We will examine in our paper:

1) Oxidative reactions taking place in alkali cellulose in the presence and absence of oxidation accelerators and retarders, in particular the action of sodium sulfite and sulfide; attention will be turned to the action of sodium sulfide in alkali cellulose, at first from the standpoint of accelerating oxidation, and then retarding it by transformation into sodium sulfite, and the effect of adding sodium sulfide to viscose in relation to oxidative transformations in alkali cellulose.

2) The relationship of cellulose xanthogenates and other sulfur compounds to oxygen; it will be graphically shown that the xanthogenates of alcohols and cellulose are oxidized to dixanthogenates, as was pointed out in our previous papers.

## EXPERIMENTAL

### 1. Influence of Anti-Oxidant Additions upon the Aging of Alkali Cellulose

The oxidation of alkali cellulose is the most suitable means for studying oxidative transformations of cellulose and has great technical significance in the ripening stage of viscose production (aging of alkali cellulose), and also in the synthesis of cellulose ethers. It should be noted that a peculiarity of oxidative phenomena in alkali cellulose, in comparison with the oxidation of cellulose in cuprammonium solutions, is the topochemical character of the reaction. The preparation of alkali cellulose itself, in which are contained compounds of variable composition formed from cellulose, alkali and water, is obtained by a topochemical process. Concerning oxidative transformations of cellulose in alkali cellulose, which are usually also accompanied by reactions of intramolecular oxidation - reduction and hydrolytic cleavage, there is a rather extensive literature, although there is still much in the aging of alkali cellulose which remains unclear. Much interest has been directed to methods of accelerating and retarding oxidative reactions in the aging of alkali cellulose, since it is often necessary in practice to regulate the rate of this oxidative transformation, for example to decrease it during the warm seasons of the year. In our experiments attention was turned to the study of several substances for the purpose of finding retarding and accelerating agents in the oxidation of alkali cellulose.

Sulfite is a known oxidation inhibitor, which is sometimes used for decreasing the aging rate of alkali cellulose on viscose fabrics, as is shown in our own and foreign literature sources. According to the data in the literature, sodium sulfide, by its valence change, can serve as an accelerator in the oxidation of alkali cellulose. However, various authors judge the accelerating and retarding action of additives in alkali cellulose by the usual indirect method - by the decrease or increase in the viscosity of viscose, which may lead to erroneous conclusions, since in a multicomponent and variable system such as viscose, various reactions with the additive introduced are possible. According to the data of Tanemura et al [6], sodium sulfite in viscose prevents cellulose from oxidizing and viscose from aging.

E. Meos-Popsueva [7] found that sodium sulfite inhibits the oxidative destruction of cellulose, if the sulfite is added at mercerization or immediately after pulverization. In this work indirect controls were carried out on the action of sulfite by determination of the viscosity of the viscose obtained from the corresponding samples of alkali cellulose i.e., not having considered the interference of sodium sulfite in the transformation of the viscose components. As for the role of sodium sulfide as an additive to alkali cellulose, the literature contains conflicting data. The study of the role of sodium sulfite and sodium sulfide in alkali cellulose and in viscose presented great difficulties and was conducted in our laboratories for many years simultaneously with works of other authors. We tested a series of substances as oxidants and antioxidants by using a direct method for calculating the course of oxidative transformations; by shaking the alkali cellulose in oxygen delivered from a burette in vessels described in our work on the study of the oxidation of cuprammonium solutions. For greater uniformity, the process of oxidation of

the alkali cellulose was carried out under uniform conditions, the vessel with the alkali cellulose was placed in a shaker, the readings for the oxygen used up were conducted in analytical burettes, and small sample weights of cellulose were taken.

For purposes of comparison parallel experiments were conducted on sulfited viscose cellulose and on well-purified linters, but very little substantial difference was observed. For the mercerization of cellulose chemically pure sodium hydroxide was used, at a concentration of 220 g per liter of caustic at a bath modulus of 1:20, time of mercerization 2 hours, coefficient of wringing equal to 3, i.e., the wringing pressure was exerted up to three times the weight of the original sample of cellulose. The alkali cellulose pressed out, amounting to 5 g, i.e. containing 1.7 g of cellulose, was immediately placed into the oxidizing flask and continuously and evenly shaken. In one series of experiments (S. N. Danilov and E. I. Geine) the following additives were compared: sodium sulfite, sodium sulfide, naphthol, a mixture of naphthol and sodium sulfite or sodium sulfide, sodium arsenite, a mixture of the latter with sodium sulfite, a mixture of sodium sulfide and sodium sulfite. The additives were introduced either in equal weights or molecular ratios, which, however, had little to do with the results. In Table 1 are given several averaged data, in which the additives introduced were 3.9% of the weight of the cellulose or 1.3% of the weight of the alkali cellulose.

TABLE 1  
Influence of Additives (1.3%) in Alkali Cellulose  
on the Absorption of Oxygen  
(Danilov and Geine)

Without additives	Oxygen consumed in 10 hours (in ml)							
	$\text{Na}_2\text{SO}_3$	$\text{Na}_2\text{S}$	$\text{NaS} + \text{Na}_2\text{SO}_3$	alpha-Napthol	alpha-Napthol + $\text{Na}_2\text{S}$	alpha-Napthol + $\text{Na}_2\text{SO}_3$	$\text{Na}_3\text{AsO}_3$	$\text{Na}_3\text{AsO}_3 + \text{Na}_2\text{SO}_3$
63	15.4	33	6.8	54	8	51	62	43

Although without additives the alkali cellulose absorbed 63 ml of oxygen in 10 hours, in the presence of sodium sulfite it absorbed only 15 ml of oxygen in the same period of time, and for the mixture of sodium sulfite and sodium sulfide only 7 ml. It should be noted that at first the sodium sulfide somewhat accelerated the absorption of oxygen, as is indicated by the absorption curve which is here omitted for the sake of brevity, and then retarded it due to its oxidation products, although this inhibition was much weaker than with sodium sulfite. It is possible that the sodium sulfide at first acted as an accelerator for the aging of the alkali cellulose until its oxidation products, among which was sodium sulfite, accumulated in some quantity (an alkaline medium prevents the separation of free sulfur). By these transformations of sodium sulfide it is possible to explain the lack of clarity in the conclusions of various investigators concerning the role of sodium sulfide in alkali cellulose and viscose. Mure and Dufress, studying the role of sulfur and sulfur compounds in the oxidation of benzaldehyde, etc., obtained somewhat contradictory results (sodium sulfide and carbon bisulfide hasten the oxidation of benzaldehyde). It is possible that, by this same reasoning, the oxidation products of the sulfur compounds may act in an opposite fashion to the original sulfur compounds (sodium sulfite retards the oxidation of benzaldehyde). Whereas the mixture of sodium sulfide and naphthol considerably retards the oxidation reaction, more



so than with each individual component, we see that the mixture of naphthol with sodium sulfite has little influence on the intensity of oxidation. This result may be explained by the fact that naphthol combines with sodium sulfite, which is favorable for oxidation with a mixture of naphthol and sodium sulfide and unfavorable for a mixture of sodium sulfite and naphthol. Although sodium arsenite does not of itself retard oxidation, mixing it with sodium sulfite partially hinders the reaction, but less than with sodium sulfite alone. This may be connected with the fact that as soon as sodium sulfite is added to the arsenite salt, both salts immediately begin to oxidize, notwithstanding the strong alkaline medium; this is a known instance of chemical induction. It must be stated that in connection with the strong oxidation retarding action of mixtures of sodium sulfite and sodium sulfide, according to the data of Mure and Dufress, sodium sulfide is an inhibitor for the oxidation of sodium sulfite. In Table 1 are given average figures for two parallel experiments, both of which gave very similar results.

Let us examine in somewhat greater detail the question of the role of sodium sulfide in the aging of alkali cellulose and in viscose. From alkali cellulose obtained in the presence of sodium sulfide, as is shown by our experiments and the experiments of other authors, viscose is obtained with a considerably lower viscosity (2.5-3 times) depending upon concentration and conditions.

This action of sodium sulfide is observed [8] only upon addition during mercerization and if the aging of the alkali cellulose is carried out in oxygen and not in an inert gas. A. Pakshver and V. Sobolieva [9] explain the lowering of the viscosity of viscose upon addition of sodium sulfide to mercerized cellulose by the supposition that sodium sulfide in alkaline medium weakens the bond between the separate cellulose chains, and this leads to a considerable lowering of the viscosity of concentrated solutions, although it was not considered that sodium sulfide may accelerate the oxidation reaction. However, the action in viscose upon the addition of sodium sulfide to mercerized cellulose is more complicated, since upon xanthogenation, the sodium sulfide which was not oxidized in the alkali cellulose should form trithiocarbonate, and the products of its oxidation, as for example, sodium sulfite, play a complex role in viscose, according to our data (1934 and later).

According to experiments [10] S. Danilov and C. Rizov) in our laboratory, sodium sulfide is absorbed by alkali cellulose in almost the same concentrations as originally present (in our experiments 10 g per liter of alkali cellulose, containing 220 g per liter of sodium hydroxide; for the experiments we used sodium sulfide with nine waters of crystallization, well purified).

To establish this fact we conducted an analysis of the alkali cellulose for the sodium sulfide content by oxidizing the alkali cellulose with alkaline hypobromite and determining the sulfur as barium sulfate.

It is of interest that the influence of sodium sulfide on the viscosity of viscose is clearly expressed only in those cases where the pre-maturing of the alkali cellulose was carried out for 20 to 40 hours, so that analogous changes in the viscosity of viscose may be obtained even without the addition of sodium sulfide if the time for pre-maturing of the alkali cellulose is increased. An unfavorable aspect of the addition of sodium sulfide is the fact that upon the introduction of even 10 g of sulfide per liter, the separation of hydrogen sulfide upon spinning is increased 15-20%.



## 2. Oxidative Action of Oxygen on Xanthogenates

### a) Treatment of Viscose with Oxygen

The components of viscose - xanthogenate and secondary sulfur derivatives - are easily oxidized by atmospheric oxygen, although cellulose itself is evidently only slightly oxidized under these conditions, since the secondary sulfur derivatives and the xanthogenate groups are first oxidized, whereupon one substance acts towards another as an inhibitor at one time and at another time as an accelerator of oxidation. It is known that the xanthogenates of alcohols retard the oxidation of benzaldehyde and sodium sulfite (Mure and Dufress), and thiosulfate accelerates the oxidation of sulfite (see the data of Danilov et al on the role of sulfite and thiosulfate in cuprammonium solutions of cellulose).

Lottermozer [11] observed that the absorption of oxygen by viscose leads to a sharp decrease in viscosity, especially at the beginning of maturation. It is possible that the observations of many authors (Heiser and Shuster, 1926; Berle, 1926; Mikoyama, 1927; Kita, 1929) on the appearance of a minimum viscosity in the first days of the aging of viscose (the contrary is expressed by S. M. Lipatov, 1929) results not only from a more complete solution of the xanthogenate, but principally as a result of the drop in the oxygen content of viscose upon agitation. Lottermozer, studying the absorption of oxygen, found that trithiocarbonate oxidizes especially easily and thus causes an absorption of oxygen by viscose.

Table 2  
Oxidation of Xanthogenate and Viscose  
(Danilov and Geine)

	Weight g	Amount of oxygen (in ml)		
		without additives	with Na <sub>2</sub> SO <sub>3</sub>	with Na <sub>2</sub> S
Pure Xanthogenate .....	12	30.6	14.8	-
Viscose .....	100	56.5	41.4	20.8

Upon oxidation of trithiocarbonate, sodium sulfite, thiosulfate, and sulfate were found, which also confirms our experiments. Upon passing air (oxygen) into viscose, according to our experiments, trithiocarbonate and other secondary sulfur derivatives as well as cellulose xanthogenate are oxidized.

Both purified xanthogenate and viscose were oxidized as well as various sulfur compounds, which may be contained in viscose (Table 2).

Both industrial and laboratory viscose were oxidized by oxygen, with and without the addition of sodium sulfite and sodium sulfide, in the oxidation apparatus affixed with the burette. The amount of absorbed oxygen was compared against a definite interval of time.

The oxidation of xanthogenate proceeded in the presence and absence of additives, but was noticeably weaker with additives, especially in the case of the addition of sodium sulfide and sulfite, even when xanthogenate and viscose prepared without removal of oxygen were used for the experiments.

Xanthogenate, purified with acetic acid and ethyl alcohol, was dissolved anew in alkali (8%) or in water. In water, 2-3% solutions were obtained,

stable for 1 to 2 days. The initial viscosity fell sharply upon oxidation. Sulfite noticeably lowers the oxidative reaction.

A certain amount of inhibitory action (to 50 and 100%) is reached by the addition of 3% sodium sulfite or sodium sulfide in the case of viscose, and especially in the case of pure xanthogenate. The rate of oxidation also depended upon the initial viscosity, but this does not interfere with the comparison of the amount of oxygen absorbed over a long period of time.

For a study of the action of oxygen on sulfur compounds which may be considered to exist in viscose, we prepared in a pure state  $\text{Na}_2\text{CS}_3$ ,  $\text{Na}_2\text{CS}_4$ ,  $\text{Na}_2\text{S}_2$ . Trithiocarbonate was oxidized by atmospheric oxygen in the same apparatus which we used for other oxidative reactions.

The trithiocarbonate was dissolved in 4% sodium hydroxide. Experiments showed that the oxidation process proceeded moderately. The oxidation limit was not reached after 26 hours; in this time, 0.009 mole of oxygen was used up for 0.12 mole of the trithiocarbonate. Upon oxidation there were obtained:  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ .

The perthiocarbonate  $\text{Na}_2\text{CS}_4$  was also oxidized in 4% sodium hydroxide. The oxidation proceeds slowly; after 26 hours only 0.01 moles of oxygen was used up for 0.12 mole of the perthiocarbonate, the reaction products found being:  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$ .

In the oxidation of  $\text{Na}_2\text{S}_2$  in 4%  $\text{NaOH}$ , a rapid absorption of oxygen took place at first; after the first hour there was absorbed 38% of all the oxygen absorbed in 20 hours. After 20 hours 0.006 mole of oxygen was absorbed for 0.12 mole of the disulfide.

We investigated the oxidation of viscose and xanthogenates in a large number of experiments in which the viscose was first held in a vacuum of 20 mm of mercury, and then kept in an atmosphere of oxygen or had a current of oxygen passed through it. In order to eliminate the error of a possibility of discharge of carbon bisulfide and in order to eliminate previously absorbed oxygen, etc., a parallel experiment was run in which a current of hydrogen was blown through the viscose, a third viscose was kept in a closed vessel without blowing any gas through. An investigation of these three groups of viscose was conducted in relationship to maturation (by the ammonium chloride number or the salt index), viscosity and the degree of xanthogen (polymer) formation, determined by the sulfur in the film according to Bernhardt. Not citing the large amount of material obtained, we will limit ourselves to drawing conclusions from these experiments.

The viscose through which oxygen was passed continuously or with interruptions for several hours and days, was differentiated from the standard viscose and from the viscose through which hydrogen was blown, in the following relationships: the passage of oxygen caused a decrease in viscosity, an increase in maturity and an increased polymer formation (by various methods). The effect of oxidation in relation to the properties of viscose is quite noticeable, although not especially great, since the oxygen is evidently directed principally towards the secondary sulfur products. Oxygen effects a more rapid decomposition of the xanthogenate, which is confirmed by an earlier hypothesis (S. N. Danilov) on the cleavage of dithiocarbonate groups as a result of an intermediate formation of the dioxanthogenide upon the oxidation of viscose. Analysis for the sodium sulfite and thiosulfate content indicated a five-ten fold increase in the amount of these salts in oxidized viscose, in which more thiosulfate was accumulated than sulfite.

To establish the protective action of pure sodium sulfite as anti-oxidant, we carried out special experiments, in which were compared standard viscose and viscose with the addition of sodium sulfite up to 30% of the weight of the cellulose, also with the addition of sodium sulfate which may arise from the sulfite, and also viscose without additives through which oxygen was passed. Maturation determinations were carried out, by means of the ammonium chloride and sodium chloride numbers and by the viscosity, for one, two and three days, and also polymer determinations by the sulfur in the film. Where sulfite was added, thiosulfate (to 50%) and some sodium sulfate were formed upon passage of oxygen. Where oxygen was not passed into the viscose, the least amount of sulfite was converted to the thiosulfate (10-15%). The formation of thiosulfate indicates the occurrence of a cleavage of sulfur by sulfite from the polysulfur compounds formed by the oxidation of viscose.

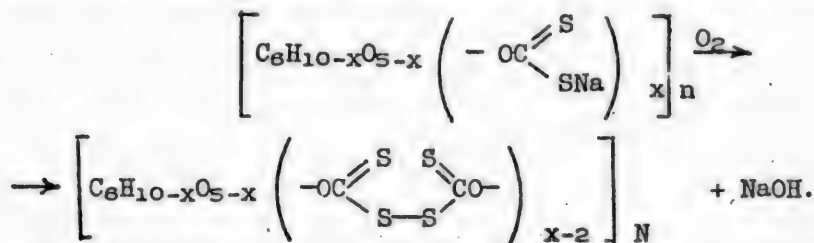
The introduction of sodium sulfite into viscose causes a lesser effect on the viscosity, maturity and polymerization of oxygen-treated viscose than when sulfite was not added.

For the determination of the polymer, in order to eliminate the interference of sodium sulfite, the xanthogenate was purified - first according to Lizer, and then, for the final removal of sodium sulfite, according to Atsuki. The polymer was also determined according to Bernhardt. In contradistinction to cuprammonium solutions of cellulose, where the anti-oxidant role of sulfite is quite significant, in viscose this role of sulfite is less marked. In our opinion, sulfite functions principally in viscose as a sulfur removing substance, similar to sodium arsenite and potassium and sodium cyanide.

#### b) Action of Oxygen on Xanthogenates

(S. N. Danilov and N. M. Grad)

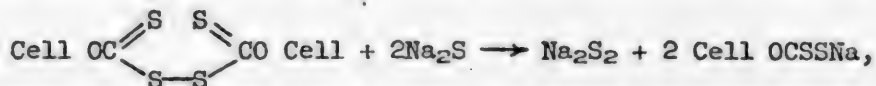
Of indirect interest is the question of the oxidation of xanthogenates by atmospheric oxygen to dixanthogenides, which was noted, in particular, in the work of S. Danilov and O. Koz'mina [12]:



Experiments on the oxidation of sodium ethylxanthogenate by oxygen were carried out in our laboratory in 1935. The data we obtained completely confirm the fact that xanthogenates form dixanthogenides comparatively easily by atmospheric oxidation. Analogous data in relation to ethyl xanthogenates were obtained by S. L. Bogdanovski (1946), although he did not separate the dixanthogenide in the pure state, since he worked with small quantities. Bogdanovski showed that the dixanthogenide of ethyl alcohol is obtained from sodium xanthogenate and not from xanthogenic acid, the presence of which, in solutions of xanthogenates as a result of hydrolysis, was admitted by earlier investigators of viscose (Cross and Biven, Heiser and Shuster).

For a more exact evaluation of the question of the formation of dixanthogenides from the oxidation of xanthogenates by oxygen, we carried out experiments of the oxidation of aqueous solutions of potassium ethylxanthogenate. The formation of the dixanthogenide may be affirmed by its ability to form sulfocyanogen ions by action with potassium cyanide, as was shown in a previous paper of ours. We conducted a series of experiments on the oxidation by oxygen of the xanthogenate of diacetoneglucose, which according to its structure is closer than the xanthogenates of monoatomic alcohols to the xanthogenate of cellulose. In an aqueous medium, the dixanthogenide formed by the hydrolytic action of water could not be separated from the oxidation products. In a chloroform solution, oxidation assured the separation of the dixanthogenide from its admixture with diacetoneglucose, obtained as a result of the readily decomposable nature of its xanthogenate derivatives. By the oxidation of cellulose xanthogenate, purified according to Atsuki, with oxygen in an aqueous medium, the dixanthogenide was obtained, but in all cases with an admixture of xanthogenate which we could not separate. The determination of the total sulfur content in the cellulose derivative obtained, i.e. sulfur, titratable with iodine (xanthogenate), and sulfur, yielding potassium cyanide (i.e., 1/4 of the dixanthogenide sulfur), indicated the possibility of the presence of both products. Experiments conducted on the oxidation of cellulose xanthogenate confirmed the fact that with increase of time of oxidation the alkalinity of the solution increases, at which the amount of cellulose dixanthogenide formed begins to decrease. It may be surmised (S.N.Danilov, O.P. Koz'mina), that upon the aging of viscose the atmospheric oxygen oxidizes cellulose xanthogenate to the dixanthogenide, which then splits off alkali with the formation of a cellulose xanthogenate, but with a lower degree of xanthogenation as a result of the decomposition of one xanthogenate group in the disulfide. The formation of dixanthogenides as a result of the oxidation of viscose should lower the stability of viscose. It has already been stated that in the oxidation of cellulose xanthogenate by oxygen the dixanthogenide is partially formed, but not with a quantitative yield, since the alkali which separates decomposes the dixanthogenide. Sodium sulfide may also decompose the dixanthogenide, and should thereby be converted to sodium disulfide.

The reductive interreaction of sodium sulfide with cellulose dixanthogenides may be considered as the source for the formation of secondary sulfur compounds (sodium disulfide), with a yellowing of the solution, according to the scheme:



but this question will be examined in greater detail in a following paper. Sodium sulfide, possibly, promotes the oxidation of cellulose xanthogenate to the dixanthogenide, and acting upon the dixanthogenide, is converted into sodium disulfide, the latter in the presence of carbon bisulfide forms the perthiocarbonate.

The oxidation of the xanthogenate of diacetoneglucose by atmospheric oxygen, conducted for a comparison with cellulose xanthogenate, was carried out in a vessel with an affixed burette. The synthesis of the xanthogenate of this sugar has been described in a previous paper of ours [13].

The dixanthogenide of diacetone glucose, obtained by the action of a 3% solution of iodine on the xanthogenate, had a m.p. of 110-111°.



### Analysis of the Dixanthogenide

0.2448 g substance: 0.3442 g BaSO<sub>4</sub>

0.2126 g substance: 0.3034 g BaSO<sub>4</sub>

Found %: S 19.28, 19.20.

C<sub>26</sub>H<sub>38</sub>O<sub>12</sub>S<sub>4</sub>. Calculated %: S 19.10.

The dixanthogenide of diacetone glucose is soluble in benzene, chloroform, ether, pyridine, with difficulty in acetone and alcohol, is not wetted with water. This product appeared identical with that which was separated by the oxidation of the xanthogenate of diacetoneglucose by oxygen.

### Preparation of the Dixanthogenide of Diacetoneglucose by the Action of Atmospheric Oxygen on the Xanthogenate of Diacetoneglucose

We conducted the following experiments with the purpose of obtaining the dixanthogenide of diacetoneglucose by the direct oxidation of the xanthogenate of diacetoneglucose by oxygen.

1) Through a solution of freshly prepared xanthogenate (from 4 g of the diacetoneglucose), dissolved in 20 ml of water, after addition of 0.03 g of sodium bicarbonate, was passed a stream of oxygen (after the entire system was filled with oxygen).

During the reaction, the reaction flask was subjected to continuous shaking (in the nature of a pendulum). After 32 hours, 86 ml of oxygen were absorbed, after which its absorption in these rather considerable quantities ceased. Theoretically, for the formation of the dixanthogenide, the absorption of 80 ml of oxygen would be sufficient. The yellow solution obtained as a result of the reaction had a sharp, unpleasant odor. The formation of a precipitate was not observed (and the dixanthogenide of diacetoneglucose is completely insoluble in water). A test with litmus and methyl orange showed that the solution obtained had an alkaline reaction. A qualitative test on the action of iodine upon the solution acidified with acetic acid also did not adduce the formation of the dixanthogenide, although a decolorization of the iodine took place. This indicated to us the absence of the original xanthogenate in the solution. From the solution obtained several extractions with ether were made, from which, after evaporation of the ether, were produced white leaflets of diacetoneglucose, m.p. 101°. Investigation of the aqueous remainder showed that it contained sulfur products from which the ions of S<sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> were absent. The S<sub>2</sub>O<sub>3</sub> ion was present. The volatile products were not investigated.

The fact that an absorption of oxygen by the reaction mixture took place showed that oxidation occurred, but the absence of a precipitate of the dixanthogenate appeared to be either the result of a decomposition of the aqueous solution of the xanthogenate, or a decomposition of the dixanthogenide formed by the action of alkali. Therefore in succeeding experiments we tried to avoid the possible action of alkali on the dixanthogenide formed.

2) To a freshly prepared solution of the xanthogenate of diacetone glucose (6 g of it) in water, to which has been added 25 ml of a 2.5% solution of acetic acid was passed a stream of oxygen for 32 hours. 87 ml of oxygen were absorbed, i.e. less than in the previous case where oxidation took place in a weakly alkaline medium. At the end of the indicated time, the organic products from the solution obtained, which did not contain a precipitate, were extracted with ether, and the original diacetoneglucose again separated with a m.p. of 102°. The aqueous solution in this case also did not contain the

xanthogenate, but contained S<sup>2-</sup> ion, which was determined by the formation of corresponding precipitates with cadmium and lead salts and by the evolution of hydrogen sulfide upon acidification.

On the basis of the results obtained from the above two experiments, we came to the conclusion that it would be necessary to try to carry out the oxidation in the medium of an organic solvent, in order to avoid the decomposing action of water on the xanthogenate of diacetoneglucose.

3) Through a freshly-prepared solution of the xanthogenate (from 10 g of the diacetoneglucose) in 50 ml of dry chloroform was passed a stream of oxygen. The absorption of oxygen in considerable quantities also ceased after 32 hours. 260 ml of oxygen was absorbed. Theoretically, 215 ml is required for the oxidation. Upon completion of the reaction, a white precipitate (2.2 g) of inorganic salts was filtered off. From the chloroform solution was separated 6.1 g of a yellow substance, m.p. 105-108°. Upon rubbing the separated substance with water in a mortar, a portion of it dissolved and left only 1.9 g of a substance, insoluble in water and even not at all wetted by water. The substance obtained had a m.p. of 110°, after recrystallization from acetone the m.p. increased to 111°. According to our and Permiakova's data, the melting point of the dixanthogenide we obtained as a result of the oxidation of the xanthogenate of diacetoneglucose with oxygen coincides with that for the dixanthogenide obtained by the action of iodine on the xanthogenate of diacetoneglucose. An ether extraction was made from the wash water (the xanthogenate, as is known, is insoluble in ether), from which 3.7 g of diacetoneglucose was separated after evaporation of the ether.

A repetition of the experiment under analogous conditions also led to the formation of a mixture of diacetoneglucose and its dixanthogenide (see Table 3).

TABLE 3

Analyses	I	II
Amount of diacetone glucose taken for the preparation of the xanthogenate (in g) .....	10	8
Amount of oxygen absorbed (in ml).....	260	218
Dixanthogenide separated (in g) .....	2.9	2.3
Regenerated diacetoneglucose (in g) .....	2.7	2.0
Yield of dixanthogenide (in %) (in relation to the original diacetoneglucose) .....	20.96	22.41

Analysis of the Dixanthogenide

0.2268 g substance: 0.3114 g BaSO<sub>4</sub>

0.2331 g substance: 0.3216 g BaSO<sub>4</sub>

Found %: S 18.83, 18.92

C<sub>26</sub>H<sub>38</sub>O<sub>12</sub>S<sub>4</sub>. Calculated %: S 19.10.

Oxidation of Cellulose Xanthogenate

For the preparation of the dixanthogenides of cellulose by the action of iodine as well as by the oxidation of cellulose xanthogenate, we started from xanthogenates precipitated from viscose, according to Atsuki [14], but using methyl alcohol instead of ethyl.

For the sake of brevity we will present only one of the experiments for the preparation of pure xanthogenate.

#### Preparation of Pure Cellulose Xanthogenate

20 g of cellulose (containing 92%  $\alpha$ -cellulose) was mercerized at a temperature of 18° for 1.5 hours with 18% alkali. Vat modulus was 1:20. The alkali cellulose was then pressed out in a hand-screw press. The weight of alkali cellulose was 62.15 g. The pressing coefficient was 3.1. After prematuring for 65 hours at a temperature of 18° the alkali cellulose was xanthogenized for 2.5 hours in a slowly-turning, thick-walled glass jar containing 5.8 ml of carbon disulfide (40% of the weight of the  $\alpha$ -cellulose). The carbon disulfide was first dried with phosphoric anhydride or calcium chloride, then distilled. The initial temperature of xanthogenation was 20°, the final temperature 30°. Upon completion of xanthogenation the xanthogenate was dissolved in weak alkali, with continuous agitation for 45 minutes.

For calculating the additives we assigned the following parameters for the composition of the viscose:

$\alpha$ -cellulose content .....	7%
total alkalinity of the viscose ...	7%

The viscose obtained under the given conditions had an infinite ripening time (according to the ammonium chloride number) and a viscosity of 42 (steel ball 0.1313 g., height 20 cm).

For preparing the xanthogenate, the viscose was neutralized with a half-normal solution of acetic acid to a weakly-acid reaction (by phenolphthalein), and then to it was added with mixing a 4-fold quantity of methyl alcohol (about 1 l.); the xanthogenate then separated as a grayish-green precipitate. After filtering on a Buchner funnel it was washed many times with methyl alcohol, after each wash being transferred to a porcelain mortar and ground with a new portion of the alcohol, then again filtered and again ground with alcohol until the alcohol, after washing, ceased to give a color reaction upon the addition of lead acetate and to decolorize iodine. After this the cellulose xanthogenate was filtered, washed with ether and dried in a vacuum desiccator over sulfuric acid for 25 hours.

The determination of sodium as  $\text{Na}_2\text{SO}_4$  was carried out by burning the xanthogenate followed by the addition of sulfuric acid.

The sulfur determination was carried out in the dixanthogenide obtained from xanthogenate (according to Kariusu), and also by the amount of iodine used for titrating the sample of xanthogenate, with a back titration of the excess iodine by sodium thiosulfate.

The determination of cellulose was carried out by the weight of cellulose separated and dried after a 5 minute boiling of the xanthogenate with 3% sulfuric acid. The analytical data are shown in Table 4.

For the preparation of the dixanthogenide of cellulose, the pure xanthogenate was dissolved in water, and in those cases where a complete solution could not be achieved, to the suspension obtained was added a small quantity of acetic acid. Then a 0.1 N solution of iodine was added until decolorization ceased. The dixanthogenide separated after 10-15 minutes as a white precipitate, which was filtered, washed with methyl alcohol and ether and dried in a vacuum-desiccator over phosphoric anhydride.

In connection with the fact that the dixanthogenide as well as the

Table 4  
Analysis of the Xanthogenate

Analyses	I	II
1. Weight of the xanthogenate (in g) .....	1.3248	1.5432
Weight of Na <sub>2</sub> SO <sub>4</sub> (in g) .....	0.1728	0.2099
Sodium content (in %) .....	4.24	4.40
2. Weight of the xanthogenate (in g) .....	1.4436	1.5208
Weight of cellulose (in g) .....	1.0516	1.1047
Cellulose content (in %) .....	72.85	72.64
3. Weight of the xanthogenate (in g) .....	2.1624	1.7367
Iodine titer 0.01301		
Amount of iodine used for the titration (in ml).	42.5	33.6
Amount of sulfur (in g) .....	0.2776	0.2202
Sulfur content (in %) .....	12.84	12.68

the xanthogenate of cellulose undergoes some decomposition upon storage, it was decided to prepare new viscose for each series of experiments performed and to precipitate the xanthogenate from it, and from the latter to prepare the dixanthogenide (Table 5).

Table 5  
Analysis of the Dixanthogenide Obtained

Analyses	I	II	Calculated
Weight of the dixanthogenide (in g) .....	0.2734	0.2444	
Weight of BaSO <sub>4</sub> (in g) .....	0.2626	0.2326	
Sulfur content (in %) .....	13.17	13.06	13.40
Weight of the dixanthogenide (in g) .....	1.3241	1.1875	
Weight of cellulose (in g) .....	0.9960	0.8883	
Cellulose content (in %) .....	75.22	74.98	76.07

Since the content of sulfur and cellulose in the xanthogenate is not constant, but depends upon a whole group of factors in the process of preparing viscose, we analyzed the xanthogenate each time and proceeded in the succeeding syntheses on the basis of its sulfur and cellulose content.

Preparation of the Dixanthogenide of Cellulose by Oxidizing  
Cellulose Xanthogenate with Oxygen

We decided not to conduct the oxidation in an alkaline medium, since there was a danger that the dixanthogenide obtained would be decomposed to xanthogenate and other sulfur-bearing decomposition products by the action of alkali.

We therefore passed oxygen through an aqueous suspension of the xanthogenate placed in a hermetically-sealed goose-neck flask. First, with shaking, the air was forced out of the goose-neck flask by the oxygen. The amount of oxygen absorbed during the reaction was determined by the reading on the burette, which was filled with water (from an attached bulb). The goose-neck flask,



which was connected with the oxygen burette, was furnished with a three-way stopcock, which was opened from time to time to the apparatus, and remained shut the rest of the time. The absorption of oxygen proceeded quickly for the first two hours, then more slowly. As indicated by qualitative tests after 4-5 hours, the sulfide group, in all probability, was not formed in noticeable quantities, which we verified by treating the reaction mixture with potassium cyanide.

Qualitative experiments which we conducted on the oxidation of potassium ethylxanthogenate and potassium butylxanthogenate showed that both immediately begin to absorb oxygen, but with different rates of speed. After 2-4 hours, we were able to observe quite distinctly the presence of the dixanthogenide in the reaction mixture obtained after oxidation of the potassium ethylxanthogenate. In the reaction mixture for the oxidation of potassium butylxanthogenate, the presence of the dixanthogenide in noticeable quantities could be observed only after 12 hours. For the xanthogenate of diacetoneglucose, the oxygen absorption was considerable and lasted 30-32 hours; therefore, we chose a time of 24 hours for succeeding experiments on the oxidation of cellulose xanthogenate.

The results obtained for two oxidation experiments are presented herewith.

From viscose with a ripeness of 22 (according to the ammonium chloride number) and a viscosity of 16, the xanthogenate was separated, containing 4.56% sulfur and 1.62% sodium. 65 ml of oxygen was absorbed.

#### Analysis

Weight of xanthogenate taken for the oxidation ( in g ) ...	10.4562
Its sulfur content (in %) .....	4.56
1) Weight of the substance obtained as a result of the oxidation of the xanthogenate (in g) .....	4.4258
Amount of silver nitrate (in ml) used for titrating the thiocyanate formed after the reaction with potassium cyanide. Titer of $\text{AgNO}_3$ (CNS') 0.005878 .....	6.6
Amount of thiocyanate (in g) .....	0.0392
Amount of sulfur separated as thiocyanate (in g) .....	0.0216
Amount of dixanthogenide sulfur ( in g ) .....	0.0864
Dixanthogenide sulfur content (in %) (in relation to the sample weight) .....	1.95
2) Weight of the product obtained as a result of oxidation ..	0.3247
Weight of $\text{BaSO}_4$ (in g) .....	0.1021
Amount of sulfur (in g) .....	0.0140
Total sulfur content (in %) .....	4.33

The data obtained show that the greater part of the sulfur in the cellulose derivative obtained is not combined as disulfide. Qualitative reactions performed on the derivative obtained show the presence of xanthogenate sulfur. Therefore, in the following experiment, we made separate determinations for xanthogenate and dixanthogenide sulfur (this experiment was described earlier in more detail).

The xanthogenate was precipitated from viscose, obtained under the below-described conditions, in an acetic acid medium by the action of methyl alcohol. The conditions for obtaining the viscose were the following:

Time of mercerization .....	1. 5 hours
Vat modulus .....	1. 20
Temperature of mercerization .....	40°

Concentration of mercerization alkali .....	222 g/l
Pressing coefficient .....	2.97
Ripening temperature .....	37°
Ripening time .....	22 hours
Amount of carbon bisulfide introduced into the xanthogenate reaction .....	40% (in relation to $\alpha$ -cellulose)

Parameters of the Viscose Obtained:

Content of xanthogenate sulfur (in %) .....	1.23
Content of remaining sulfur (in %) .....	0.47
Ripeness (by ammonium chloride number) .....	35
Viscosity .....	62
Content of $\alpha$ -cellulose .....	7.8
Alkalinity of the viscose (in %) .....	7.2

After numerous washings with alcohol along with rubbing in a mortar (until decolorization of iodine ceased), the xanthogenate was obtained with a sulfur content of 5.62%, sodium 1.94%.

A sample weight of the xanthogenate (12.2783 g) was suspended with a small quantity of water (in which the water solution obtained had a neutral reaction) and subjected to oxidation, under the conditions described in the previous experiment, by oxygen for 24 hours; 88 ml of oxygen were absorbed, the absorption not having been quite complete, which in all probability is related to the almost parallel course of oxidation of the xanthogenate groups of cellulose. Theoretically, 56 ml were required for the oxidation of the xanthogenate sulfur.

As a result of this reaction the cellulose derivative lightened considerably (became whiter). After its filtration from water, which showed an alkaline reaction litmus, the precipitate was washed several times with alcohol and ether. The aqueous portion of the reaction mixture did not contain xanthogenate. After the cellulose derivative was obtained, the following experiments were performed:

1) To 4.3426 g of the oxidation product obtained in a weak acetic acid solution was added iodine to the appearance of a blue color in the presence of starch; 13.3 ml of the iodine solution was used up in the titration; the dioxanthogenide remained in the precipitate;

2) To 3.4634 g of the oxidation product obtained was added an aqueous solution of 0.3 g of potassium cyanide, and the reaction mixture allowed to stand 10-12 hours, after which the cellulose derivative and the unreacted cyanide ion were precipitated with cobalt nitrate; in the filtrate obtained, the presence of thiocyanate was determined qualitatively and quantitatively; inasmuch as it is known that the original cellulose xanthogenate does not enter into side reactions, this result indicates the presence of cellulose dioxanthogenide obtained as a result of the oxidation of xanthogenate by oxygen.

The data presented below indicate that as a result of the oxidation reaction, cellulose dioxanthogenide was evidently partially formed (from 50 to 60%), taking into account that it does not react 100% with potassium cyanide.

Analysis

1) Weight of xanthogenate taken for oxidation ( in g ) .....	12.2783
Its sulfur content (in %) .....	5.62
2) Weight taken of the product obtained after oxidation (g) .	0.4364
Weight of BaSO <sub>4</sub> (in g) .....	0.1757

Its sulfur content (in g) .....	0.0241	(in % 5.52)
3) Weight taken for the iodine titration of the product obtained after oxidation (in g) .....	4.3246	
Amount of iodine used up (in ml).....	13.3	
Iodine titer 0.01301		
Amount of xanthogenate sulfur (in g) .....	0.0873	(in % 2.019)
4) Weight taken for the reaction with potassium cyanide, of the product obtained after oxidation (in g).....	3.4634	
Amount of silver nitrate used for the titration of the thiocyanate formed (in ml) .....	6.4	
Titer of $\text{AgNO}_3$ (CNS') = 0.005878		
5) Amount of thiocyanate (in g).....	0.0376	
Amount of sulfur split off (in g) .....	0.0208	(in %) 0.6
Amount of dixanthogenide sulfur (in %) .....	2.4	
Amount of dixanthogenide sulfur in the product obtained after oxidation of the xanthogenate by oxygen (by the thiocyanate formation in %) .....	43.44	
Amount of xanthogenate sulfur in the product obtained after oxidation (in %) .....	36.57.	

Consequently, in all the experiments we conducted on the oxidation of cellulose xanthogenate, we were not able to obtain a single dixanthogenide without an accompanying xanthogenate, since in all probability, if the oxidation of the xanthogenate were to go to completion, then as a result of the action of the separated alkali upon the dixanthogenide a portion of the latter would inevitably be reconverted to the xanthogenate and other sulfur products. The formation of alkali is confirmed by the fact that while the aqueous suspension of the xanthogenate (insoluble in water) showed a neutral reaction up to the oxidation, upon completion of the oxidation reaction it began to have a definite alkaline reaction (to litmus).

Although we could not isolate a single dixanthogenide of cellulose as a result of oxidation, we believe that conclusive evidence has been shown for the formation, during the process of oxidation, of a cellulose compound containing disulfide groups. Strictly speaking, this also had taken place in the oxidation of potassium ethyl xanthogenate by oxygen and in the oxidation of diacetoneglucose, but in those cases both products could be more easily separated on the basis of their sharply differing solubility in water.

#### SUMMARY

1. The oxidation of alkali cellulose was studied in the presence of various additives, retarding and accelerating oxidation. Sodium sulfite or a mixture of it with sodium sulfide shows a definite retarding action on the oxidation of alkali cellulose. Sodium sulfide alone does not have as marked an action as an anti-oxidant for alkali cellulose, since it evidently acts as an oxidation accelerator at first, and then its accumulated oxidation products begin to retard oxidation.

The action of sodium sulfite and sodium sulfide in viscose, especially by the action of air upon the latter, is very complex, since these salts also function as sulfur-removing substances.

2. It is shown that the xanthogenates of ethyl alcohol, diacetone glucose and cellulose form dixanthogenides by the action of oxygen.

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# NEW DERIVATIVES OF DISULFONES

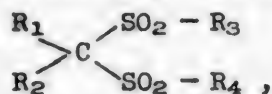
## I. HOMOLOGS AND ANALOGS OF SULFONAL

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All-Union Scientific Chemico-Pharmaceutical Institute, Moscow

Among the disulfones of the aliphatic series, Baumann and Kast [1] had found compounds (sulfonal, trional, etc.), which after a long period of time, had been considered the best of all known soporific agents.

The structure of these compounds are expressed by the general formula:

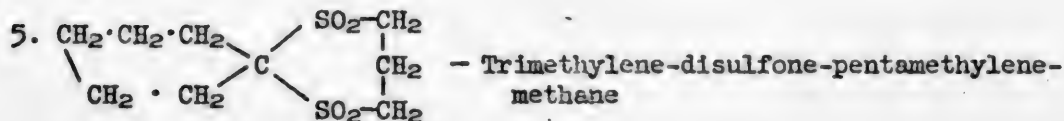
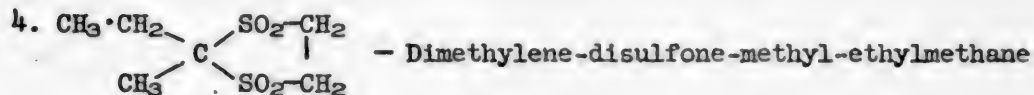
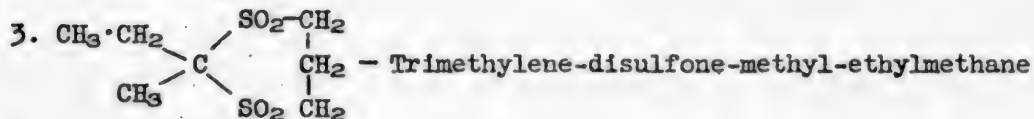
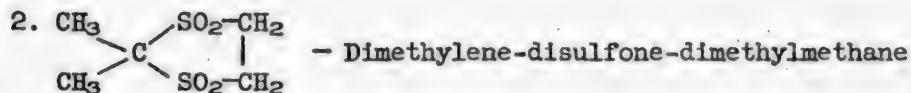
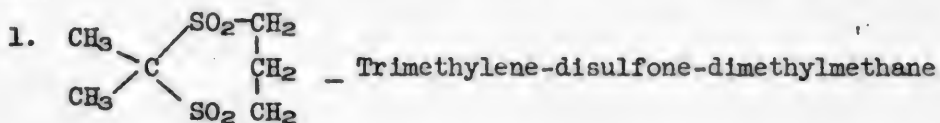


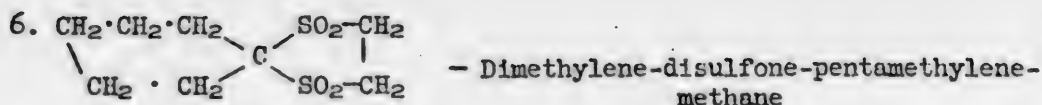
where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are alkyl radicals.

According to Kast and Baumann, they possess excellent soporific action in those cases where not less than two ethyl groups are present.

The high medicinal quality of these derivatives of disulfones, and the almost complete absence of toxicity of these derivatives induced us to make a study of new compounds in this field which may possess interesting properties.

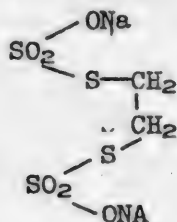
We obtained the following compounds, related to the group of cyclic disulfones:



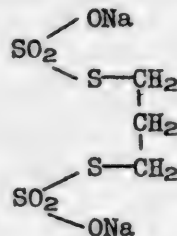


The first of these was described by Autenrieth [2] and was prepared from acetone and trimethylenemercaptan. For obtaining our preparations, we started from mercaptans obtained from dibromomethane and chlorobromotrimethylene. By the action of dibromoethane and chlorobromotrimethylene on a strong aqueous solution of hyposulfite, we obtained the corresponding:

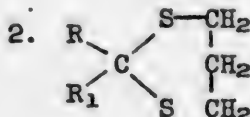
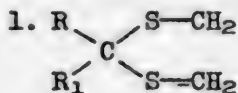
Dimethylene-dithiosulfate



Trimethylene-dithiosulfate



By the action on the compounds of the corresponding ketones in the presence of alcohol, containing about 15% hydrogen chloride, we obtained mercaptols, the structures of which correspond to the formulas:



The sulfides (mercaptols), obtained as a result of the condensation of different ketones with mercaptans, are in most part distinguished by the absence of a constant boiling point. Thus, according to Baumann [3], the mercaptol obtained from acetone and ethylmercaptan begins to boil at 80° at atmospheric pressure. The temperature in the vapors continuously increases during distillation and finally reaches 192°.

We distilled the mercaptol obtained from ethylmercaptan and cyclopentanone. The distillation was conducted in a vacuum with a residual pressure of 32-35 mm of mercury. The mercaptol began to distill at 118° in the vapors and ceased distilling at 152°. Separate portions of the distillate were then oxidized and gave identical disulfones. The disulfones, as a rule, were obtained by gently oxidizing the mercaptols with permanganate. All these compounds are difficultly soluble in water, insoluble in cold chloroform and dichloroethane, difficultly soluble in cold and easily soluble in hot ethanol. Recrystallization from hot alcohol may be used as a method of their purification. The disulfones with ethylene chains form thin needles. The disulfones with trimethylene chains form thick, well-shaped, hexahedral prisms. The trimethylene compounds melt at a temperature above that of the ethylene compounds.

## EXPERIMENTAL \*

### I. Trimethylene-dithiosulfate

Into a wide-necked jar, of 3 l. volume and furnished with a mechanical stirrer, was poured 248 g (1 M) of hyposulfite and 150 ml of water was added.

\* Our analytical records were lost during the war. We will present only the analyses of the final products, by chance left intact.

The stirrer was operated for 10 minutes, after which 238 g (1.5 M) of chlorobromotrimethylene was added. The jar was placed in a water bath. The temperature in the bath was kept between 40-45° during the course of the reaction. The reaction lasted 60-80 hours. The number of revolutions of the stirrer was about 500 per minute, thanks to which an excellent mixing of the two layers in the jar was attained. After 15-20 hours a mass of crystals of trimethylenedithiosulfate began to appear as separate clusters, the amount of which continuously increased.

At the conclusion of the reaction the precipitate was separated from the liquid portion by filtration. The filtrate was transferred to a separatory funnel, where the excess chlorobromotrimethylene was separated from the aqueous layer. The aqueous layer consisted principally of unreacted hyposulfite, sodium bromide and chloride. Trimethylenedithiosulfate was completely absent since it was salted out from water by the mineral salts. About 135 g of dithiosulfate was obtained, which was an approximately 86% yield of the theoretical. The product was easily soluble in water, difficultly soluble in hot alcohol.

## II. Mercaptol from Acetone and Trimethylenedithiosulfate

Into a wide-necked, liter jar with a glass stopper was poured 109 g (0.35 mol) of trimethylenedithiosulfate ground to a fine powder, 20 g (0.35 mol) of acetone added, and with external cooling and frequent shaking 250 g of alcohol, containing 15% hydrogen chloride gas, was added. The contents of the jar were energetically shaken every 15-20 minutes for 6 hours, after which the jar was allowed to stand until morning.

In the morning the contents of the jar, consisting of a solution of the mercaptol in alcohol and a precipitate of mineral salts, were poured into 2 liters of cold water and the emulsion formed allowed to stand until the next day. Two layers formed: below, the mercaptol which had settled, above, the solution of mineral salts. The mercaptol was separated from the aqueous layer in a separatory funnel, washed two-three times with water to a weakly-violet color to Congo red. The moist mercaptol obtained was then dried with calcium chloride or anhydrous sodium sulfate. About 30 g of the mercaptol was obtained. The yield of the mercaptol was 58% of the theoretical. Sp. Gr. at  $d^{18} = 1.12$ .

## III. Oxidation of Mercaptol to Trimethylenedisulfonedimethylmethane

The reaction sequence is shown in the table.

Ingredients	Added					
	At start	After				
		1 hour	1 hour	1 hour	6 hours	Total
Water .....	0.8 l	—	—	—	—	0.8 l
Potassium permanganate ....	16 g	8 g	8 g	8 g	4 g	44 g
Mercaptol.....	5 g	4 g	4 g	3 g	—	16 g
25% Acetic Acid.....	15 g	7 g	7 g	7 g	2 g	38 g

The oxidation was conducted at room temperature in a jar furnished with a mechanical stirrer. The number of revolutions of the stirrer was about 500 per minute.

At the conclusion of the oxidation the reaction mixture was transferred to a Buchner funnel; the manganese dioxide was filtered from the liquid and then treated twice with boiling water. The first time 250 ml was used, the

second time 150 ml. The disulfone settled out from these extracts after cooling. It was filtered off and the filtrate so obtained combined with the filtrate obtained after filtration of the manganese dioxide, and this liquid evaporated to one quarter its initial volume. A small quantity of crystals again settled out from the evaporated liquid after cooling. The crystals were collected, boiled with 150 ml of water for 20 minutes in the presence of 2 g of activated charcoal. The yield of pure preparation was 18 g. M.P. 246-248°.

Found %: S 29.91, 30.45.  
 $C_6H_{12}O_4S_2$ . Calculated %: S 30.19.

#### IV. Mercaptol from Methyleneethylketone and Trimethylenedithiosulfate

Into a wide-necked liter flask was poured 109 g (0.35 mol) of trimethylenedithiosulfate, then 25 g (0.35 mol) of methyleneethylketone and 250 g of alcohol containing 15% hydrogen chloride gas were added. The process was conducted under the same conditions as for the preparation of mercaptol from acetone. 29 g of the mercaptol was obtained,  $d^{18}_4 = 1.07$ .

#### V. Oxidation of Mercaptol to Trimethylenedisulfonemethylene methane.

15 g of the mercaptol, obtained from methyleneethylketone, was oxidized with 50 g of potassium permanganate. For neutralizing the alkali formed, 45 g of 25% acetic acid was added, in portions. 1 liter of water was used to dissolve the permanganate. The process was conducted under the conditions shown for the preparation of trimethylene-disulfone-dimethylmethane. The yield of the preparation was equal to 12 g. M.p. 204°.

Found %: S 27.92, 28.14.  
 $C_7H_{14}O_4S_2$ . Calculated %: S 28.32.

#### VI. Mercaptol from Cyclohexanone and Trimethylene-dithiosulfate

Into a half-liter jar were added successively 72 g (0.23 mol) of trimethylene-dithiosulfate, 20 g (0.2 mol) of cyclohexanone and 175 g of alcohol containing 15% hydrogen chloride. The process is conducted as described for the preparation of the mercaptol from acetone. 23 g of the mercaptol was obtained.

#### VII. Oxidation of the Mercaptol to Trimethylenedisulfonepentamethylenemethane

19 g of the mercaptol, obtained from cyclohexanone, was oxidized with 43 g of potassium permanganate. During the process 39 g of 25% acetic acid was added in portions. The water used was about 0.8 liter. The process was conducted under the conditions described for the oxidation of the mercaptol from acetone. The yield of the preparation was 12 g. M.p. 200-201°.

Found %: S 25.34, 25.46  
 $C_9H_{16}O_4S_2$ . Calculated %: S 25.40.

#### Preparation of Cyclic Disulfones from Dibromoethane

##### I. Dimethylenedithiosulfate

Into a 3 liter, wide-necked jar, furnished with a mechanical stirrer, was added 248 g (1 mol) of crystalline hyposulfite, 282 g (1.5 mol) of dibromoethane and 150 ml of water. The reaction was conducted under the same conditions as for the preparation of trimethylenedithiosulfate. The same temperature control was retained. The yield of the preparation was about 130 g. (87% of the theoretical).



## II. Mercaptol from Acetone and Dimethylenedithiosulfate

Into a half-liter jar with a glass stopper was poured 69 g (0.23 mol) of dimethylenedithiosulfate, then there were successively added 14 g (0.25 mol) of acetone and 110 g of alcohol containing 15% hydrogen chloride. The conditions of operation are the same as for the preparation of the mercaptol from the trimethylene chain. 16.5 g of the mercaptol was obtained.

## III. Oxidation of Mercaptol from Acetone

15 g of the mercaptol were oxidized with 45 g of potassium permanganate. 0.8 liter of water and 40 g of 25% acetic acid were used. The operating conditions were the same as for the preparation of the disulfone from the trimethylene chain. Yield 12.5 g. M.p. 240-242°.

Found %: S 32.09, 32.43.

$C_5H_{10}O_4S_2$ . Calculated %: S 32.32.

## IV. Mercaptol from Methyl ethyl ketone and Dimethylenedithiosulfate

To 72 g of dimethylenedithiosulfate was added 18 g of methyl ethyl ketone, and 90 g of alcohol containing 15% hydrogen chloride gas. 16 g of the mercaptol was obtained;  $d^{18} = 1.02$ .

## V. Oxidation of the Mercaptol to Dimethylenedisulfonemethyl ethyl methane

16 g of the mercaptol was oxidized with 55 g of potassium permanganate; 50 g of 25% acetic acid was used; the water taken was 1 liter. 17 g of the disulfone was obtained. M.p. 124-125°.

## VI. Mercaptol from Cyclohexanol and Dimethylenedithiosulfate

To 72 g (0.24 mol) of dimethylenedithiosulfate were added successively 22 g (0.23 mol) of cyclohexanone and 110 g of alcohol containing 15% hydrogen chloride gas. 30 g of the mercaptol was obtained.

## VII. Oxidation of the Mercaptol to Dimethylenedisulfonehexamethylene

For the oxidation of 26 g of the mercaptol, 62 g of potassium permanganate, 5 g of 25% acetic acid and 1.2 liter of water were used. 11 g of the preparation was obtained. M.p. 165-166°.

Found %: S 26.68, 27.03.

$C_8H_{14}O_4S_2$ . Calculated %: S 26.83.

I wish to express my gratitude to the director of the laboratory, Prof. O. Yu. Magidson, for his valued advice and instruction, of which I made use in the fulfillment of the present work.

### SUMMARY

1. Six cyclic disulfones were obtained, of which 5 have not been described in the literature.
2. Methods for the preparation of the cyclic disulfones have been described.

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## NEW DERIVATIVES OF DISULFONES

### II. HOMOLOGS AND ANALOGS OF SULFONAL

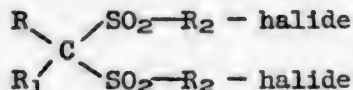
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All-Union Scientific Chemico-Pharmaceutical Institute, Moscow.

In 1891 Autenrieth obtained chloroderivatives of diethylsulfonedimethylmethane [1], starting from monochloroacetone, since preparations of the disulfone by direct halogenation were unattainable. The author expected that the chlorine would be mobile in this compound, and therefore, that by the substitution of chlorine it would be possible to obtain a new series of derivatives. This expectation was not realized; the chlorine proved to be immobile and unable to take part in double decomposition reactions.

#### Chloroderivatives of Disulfones with Open Chains

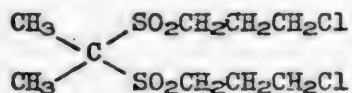
We turned our attention to the problem of obtaining a compound which would hold the halide not in the ketone group, but in the mercaptan group, i.e., a disulfone of the type:



Inasmuch as the R<sub>2</sub>-halide is a substituted alkylhalide, it may be supposed that such a substance would possess narcotic properties. We also considered that such halide compounds would be capable of double decomposition reactions, which would make possible the preparation therefrom of a new series of compounds.

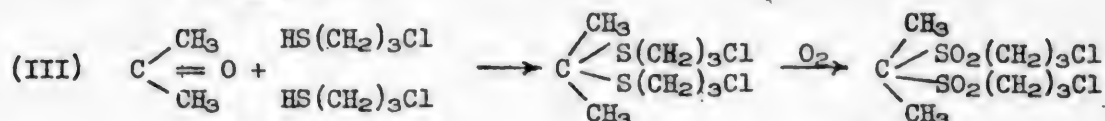
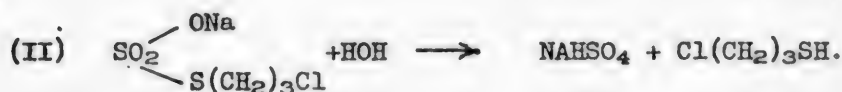
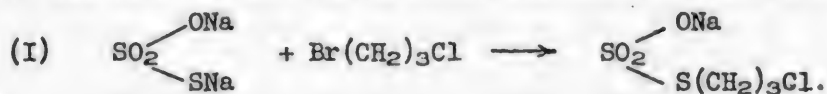
The cyclic derivatives of disulfones which we obtained previously were found to be difficultly soluble in cold water.

Concerning the mobility of the halide, compounds had to be considered which were easily soluble in cold water, or which were of the amine chlorhydrate type or the alkali salt of carbonic acid type. We were faced with the following problem: from the simplest ketone of the fatty series - acetone, and from chlorobromotrimethylene which contains dissimilar halides, to obtain di-(chloropropyl)-disulfonedimethylmethane:



In paper I it was shown that by the action of sodium thiosulfate with chlorobromotrimethylene, notwithstanding the various reaction possibilities of the halide atoms, we obtained at all times only cyclic compounds. To obtain halide-containing compounds of an acyclic nature we conducted the condensation reaction of thiosulfate and chlorobromomethylene not at 40-42°, but at 18-20°. It was decided to lengthen considerably the time of reaction; instead of 60-80 hours, the reaction process lasted 180-200 hours; but even this proved to be inadequate; the yield of the acyclic compound was only a small percentage of the

theoretical. And only when, besides using lower temperatures, we began to take not less than 6 molecules of chlorobromotrimethylene for every molecule of thiosulfate did we succeed in considerably increasing the yield of chloropropylthiosulfate. The conversion from the latter to dichloropropyl disulfone-dimethylmethane, which we will from now on call "dichloride" for the sake of brevity, was accomplished in the usual fashion according to the scheme:



The oxidation of the halidemercaptol, in contradistinction to cyclic mercaptols, takes place slowly; it is necessary to resort to increasing the temperature of the reaction mixture near the end of the oxidation, not, however, above 40°.

The "dichloride" is a solid substance, easily soluble in chloroform, dichloroethane, benzene, toluene, acetone and sulfuric ether; difficultly soluble in cold alcohol, easily in hot, from which it recrystallizes.

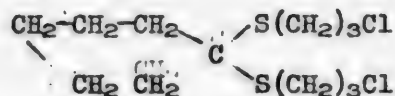
The 'dichloride' we obtained possesses all the properties characteristic of dihalide compounds of saturated hydrocarbons; it reacts with primary and secondary amines, it gives quaternary ammonium bases with tertiary amines; with potassium or sodium cyanide it gives nitriles; in certain cases, however, the course of the reaction does not, as we will see later, coincide with the usual course of reaction.

Starting from the 'dichloride' we obtained the following series of compounds:

Exp. No.	Starting Materials		Compounds obtained
1.	'Dichloride'	Aniline	N,N'-di-(phenylaminopropyl)-disulfone-dimethylmethane: $\begin{array}{c} \text{CH}_3 \quad \text{SO}_2[(\text{CH}_2)_3\text{NHC}_6\text{H}_5] \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{CH}_3 \quad \text{SO}_2[(\text{CH}_2)_3\text{NHC}_6\text{H}_5] \end{array}$
2.	'Dichloride'	Diethylamine	Chlorhydrate-γ,γ'-di-diethylaminodipropyl-disulfone-dimethylmethane $\begin{array}{c} \text{CH}_3 \quad \text{SO}_2(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2 \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{CH}_3 \quad \text{SO}_2(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2 \end{array} \cdot 2\text{HCl}$
3.	'Dichloride'	Sodium p-acetamino-phenolate	γ,γ'-di-p-acetamino-phenoxypropyl-disulfone-methane $\begin{array}{c} \text{CH}_3 \quad \text{SO}_2[(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{NHCOC}_6\text{H}_5] \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{CH}_3 \quad \text{SO}_2[(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{NHCOC}_6\text{H}_5] \end{array}$

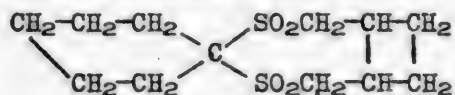
Exp. No.	Starting materials		compounds obtained
4.	'Dichloride'	Potassium cyanide	$\gamma, \gamma'$ -di-(nitrile-propyl)-disulfone-dimethylmethane $\begin{array}{c} \text{CH}_3 \quad \text{SO}_2[(\text{CH}_2)_3\text{C}\equiv\text{N}] \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{SO}_2[(\text{CH}_2)_3\text{C}\equiv\text{N}] \end{array}$
5.	$\gamma, \gamma'$ -di(nitrile-propyl)-disulfone-dimethylmethane	Sulfuric acid	$\gamma, \gamma'$ -di-(carboxy-propyl)-disulfone-dimethylmethane: $\begin{array}{c} \text{CH}_3 \quad \text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \end{array}$
6.	$\gamma, \gamma'$ -di(carboxy-propyl)-disulfone-dimethylmethane	Methanol	$\gamma, \gamma'$ -di-(carbo-methoxy-propyl)-disulfone-dimethylmethane $\begin{array}{c} \text{CH}_3 \quad \text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_3 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_3 \end{array}$
7.	'Dichloride'	Potassium hydroxide or sodium hydroxide	1,2-cyclobutylene-dimethylene-disulfonedimethylmethane: $\begin{array}{c} \text{CH}_3 \quad \text{SO}_2\text{CH}_2\text{CHCH}_2 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{SO}_2\text{CH}_2\text{CHCH}_2 \end{array}$

Also, from sodium thiosulfate, chlorobromotrimethylene and cyclohexanone, the disulfide was obtained:

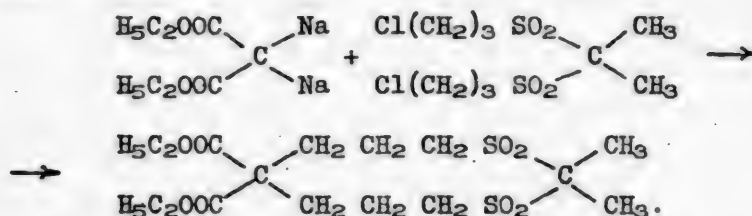


which, after oxidation, gave di-(chlor-propyl)-disulfone-pentamethylenemethane.

Upon treatment of this compound with caustic alkali, 1,2-cyclobutylene-dimethylene-disulfone-pentamethylene-methane was obtained:



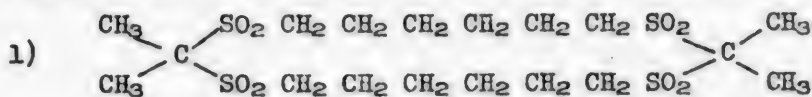
We also carried out the condensation of the 'dichloride with disodium malonic ether, having in mind the preparation of cyclic compound of the type shown below:



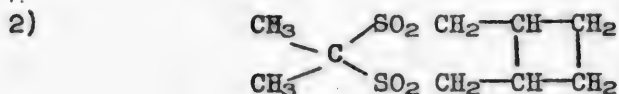
A substance was obtained with a m.p. of 139-140° and containing 25.72% of sulfur instead of 15.58%, as calculated for the expected cyclic compound. A qualitative test indicated the absence of halides and unsaturated bonds.



On the basis of these data it could be supposed that the reaction between the 'dichloride' and disodium malonic ether took place without the participation of the malonic ether and led to the formation of one of the following compounds:



Sulfur content 25.2%



Sulfur content 25.4%

In order to choose between these two formulas experiments were conducted in which instead of metallic sodium, alcoholic and strong aqueous solutions of potassium hydroxide were used. In these experiments the same substance was obtained with a m.p. of 139-140°.

Upon this basis it may be considered that the reaction took place according to the second scheme, and the substance obtained has the structure 1,2-cyclobutylene-dimethylene-disulfone-dimethylmethane.

## EXPERIMENTAL

### I. $\gamma$ -Chloro-propyl-thiosulfate

Into a 5 liter, wide-necked jar, furnished with a mechanical stirrer, were placed 496 g (2 mol) of thiosulfate and 300 ml of water; the stirrer was operated for one-half hour and then 1900 g (12 mol) of chlorobromotrimethylene and 500 ml of alcohol were added. The speed of the stirrer was 500 revolutions per minute. The reaction was continued for 180-200 hours at room temperature. At the end of the reaction the contents of the jar were transferred to a separatory funnel, where the top water-alcohol solution of  $\gamma$ -chloropropylthiosulfate was separated from the lower layer of excess chlorobromotrimethylene. To the water-alcohol layer were added another 2 liters of 95% alcohol. Thereupon about 120 g of unreacted thiosulfate separated; after which a considerable quantity of sodium bromide separates.

This quantity of alcohol is added so that the distillation of the solution in vacuo at 15-20 mm begins at 30° and ends at a temperature not higher than 45° in the bath. This is very essential, in as much as in this way there is obtained a product which is not subject to even partial decomposition. Only when the distillate begins to come over in slow drops is the temperature of the bath raised to 50-55°, by which a complete vacuum-drying of the substance obtained is achieved.

About 280 g of absolutely dry chloropropylthiosulfate was obtained. About 240 g of anhydrous hyposulfite entered into the reaction. Figuring on hyposulfite, the yield was about 86% of the theoretical. The separated layer of excess chlorobromotrimethylene was used again in the reaction.

### II. Mercaptol from Acetone and $\gamma$ -Chloropropylthiosulfate

Into a wide-necked liter jar with a glass stopper was poured 212 g of pulverized  $\gamma$ -chloropropylthiosulfate, then with agitation were added in succession

40 g of acetone and 370 g of alcohol, containing 15% hydrogen chloride. Upon addition of the alcohol, the jar was externally cooled in order that the temperature in the reaction mixture not be raised above 30°, to avoid side reactions. After addition of all the materials, the contents of the jar were energetically shaken by hand every 15-20 minutes, in order to avoid a separation of the layers in the reaction mixture. This periodic shaking was carried out for six hours. The jar with its contents was then allowed to stand quietly overnight. In the morning the contents of the jar, consisting of an alcoholic solution of the mercaptol and a precipitate of mineral salts, were poured into 2 liters of cold water, and the emulsion formed allowed to stand until the following day. Two layers were formed: below - the separated mercaptol, above - the solution of mineral salts. The mercaptol was carefully separated in a separatory funnel from the aqueous layer and then washed 2-3 times with water to a weak-violet color to Congo red, after which the moist mercaptol was dried with calcium chloride or anhydrous sodium sulfate. 69-70 g of the mercaptol were obtained, which is a yield of 54% of the theoretical;  $d^{18} = 1.12$ .

### III. Di-(chloropropyl)-disulfonedimethylmethane ('Dichloride')

Into a wide-necked, 3-liter jar, placed in a cold-water bath and furnished with a mechanical stirrer, were placed 1 liter of water and 25 g of potassium permanganate. The agitator was operated for several minutes until the permanganate was dissolved; then slowly, to avoid a strong evolution of heat, and with very careful mixing, all of the mercaptol and 35 g of a 25% aqueous solution of acetic acid were added, by means of a funnel. After reduction of the permanganate, 10 g of finely-ground permanganate and 8-10 g of 25% acetic acid were added periodically. At the beginning the reduction takes place quickly, and the additions were made every 45-60 minutes. Towards the end of the reaction the reduction took place very slowly. In total, the oxidation takes about 50 hours. Toward the end of the reaction the temperature in the bath reached 40°. Altogether, 170 g of potassium permanganate and 155 g of 25% acetic acid were used for oxidizing 70 g of the mercaptol.

At the end of the reaction, which was judged by the time taken (10-12 hours) for the potassium permanganate to remain unreduced, a little sodium bisulfite was added to the jar to reduce the excess permanganate and then 150 ml of dichlorethane or chloroform was added to extract the 'dichloride' from the reaction mixture, which is easily soluble in the cold in these solvents. Impurities, (principally cyclic disulfones) are completely insoluble in the cold in these solvents. By this method a rather pure product was extracted. After addition of the solvent the agitator was operated for a half-hour. The reaction mixture was then transferred to a Buchner funnel, the filtrate separated and poured into a separatory funnel; in the funnel the chloroform layer was separated from the aqueous, after which the solvent was distilled from the chloroform layer. 37-40 g of the 'dichloride' were obtained, or 44-46% of the theoretical.

A very pure product was obtained by boiling the 'dichloride' for 30 minutes with double its quantity of 95% alcohol in the presence of activated carbon which is 5% of the weight of the 'dichloride'. The hot alcoholic solution is filtered from the carbon. Upon standing, white odorless needles of the 'dichloride' separated from the solution. M.p. 77-78°.

Found %: S 20.17, 20.33.

$C_9H_{18}O_4S_2Cl_2$ . Calculated %: S 19.69.

### Chlorhydrate $\gamma, \gamma'$ -(Diethylamino-dipropyl)-disulfone-dimethylmethane

Into a 250 ml, round-bottomed flask, fitted with a sturdy reflux condenser,

were introduced 50 g of diethylamine mixed with 50 g of toluene, then 15 g of di-( $\gamma$ -chloropropyl)-disulfone-dimethylmethane was added. The flask was heated on a water bath at 80-90°. The mixture was kept boiling the whole time. The reaction continued for 65-66 hours.

At the completion of the reaction the toluene solution was filtered from the diethylaminechlorhydrate. The free diethylamine was then distilled from the filtrate, after which the flask with the toluene solution of the substance obtained was allowed to stand in cold water. A stream of hydrogen chloride gas was passed through the toluene solution until the free gas began to separate. As a result of this operation, the impure chlorhydrate separated. The precipitate was drawn off by suction and dissolved in double its quantity of 95% alcohol. The alcoholic solution was boiled for 30 minutes in the presence of 1 g of activated carbon, after which the hot solution was separated from the carbon. Half the solvent was distilled from the filtrate; the remaining solution was placed in a desiccator over sulfuric acid. After several hours the amine chlorhydrate separated out. The preparation was hygroscopic. White needles were obtained. The yield of the pure preparation was 11.5 g, 53% of the theoretical. M.p. of the chlorhydrate is 206-210°, with decomposition. Easily soluble in water, ethanol and chloroform.

Found %: N 6.02, 6.06; S 13.89, 13.99.

$C_{17}H_{40}O_4N_2Cl_2S_2$ . Calculated %: N 5.90; S 13.59.

The remainder is an oil, soluble in all the usual organic solvents.

#### N,N'-Di-(phenylaminopropyl)-disulfonedimethylmethane

Into a small, 100 ml flask fitted with a reflux condenser were poured 7 g of aniline and 30 g of toluene; then with shaking 5 g of di-( $\gamma$ -chloropropyl)-disulfonedimethylmethane was added. The mixture was brought to boiling, the temperature in the bath being 110-120°. The reaction was continued for about 120 hours. The end of the reaction was determined approximately by the amount of aniline hydrochloride separated.

The technical product obtained was purified in the following fashion: the toluene was distilled off and the precipitate was washed with cold ethyl alcohol until no aniline or traces of toluene were noticed. A solid residue of a light-brown color was obtained. It was treated twice with boiling alcohol, each time for twenty minutes in the presence of activated carbon. 2.5-3 g of a pure white base were obtained. The yield was 37-44% of the theoretical. M.p. 136-138°. The base forms white needles; easily soluble in chloroform, acetone, ethyl ether, benzene, almost insoluble in cold alcohol, easily in hot.

Found %: N 6.30; S 14.61.

$C_{21}H_{20}O_4N_2S_2$ . Calculated %: N 6.39; S 14.61.

#### IV. $\gamma,\gamma'$ -Di-(p-acetaminophenoxypropyl)-disulfone-dimethylmethane.

Into a 200 ml flask, fitted with a reflux condenser, were introduced 3 g of potassium hydroxide and 60 g of absolute alcohol. The mixture was heated to boiling; the solution allowed to stand and filtered. To the filtrate was added 8 g of di-( $\gamma$ -chloropropyl)-disulfonedimethylmethane. The reaction mixture was brought to boiling, which was continued for 15 hours. Then the alcohol was distilled off, after which the residue was treated with hot chloroform, the chloroform solution filtered and the solvent distilled. The solid residue was boiled for a half hour with 100 ml 95% alcohol in the presence of 1 g of activated carbon. The hot alcoholic solution was filtered from the carbon and to the

filtrate was added 150 ml of cold water. 7-8 g of the product separated. The product forms light, cream-colored flakelets; m.p. 142-144°. The compound is difficultly soluble in hot water; poorly soluble in cold alcohol, easily in hot alcohol and chloroform; insoluble in ether, benzene, and dilute hydrochloric acid.

Found %: S 11.74, 11.82.

$C_{25}H_{34}O_8N_2S_2$ . Calculated %: S 11.55.

#### V. 1,2-Cyclobutylene-dimethylene-disulfone-dimethylmethane

5 g of di-( $\gamma$ -chloropropyl)-disulfone-dimethylmethane and 2 g of potassium hydroxide were dissolved in 40 ml of alcohol. This mixture was boiled for 6 hours. A precipitate separated. After recrystallization from water, 2.5 g of a pure product was obtained, m.p. 139-140°, the yield being 64% of the theoretical. This same product with a m.p. of 139-140° was obtained also without alcohol, by the action of a 10% aqueous solution of potassium hydroxide under the same conditions.

Found %: S 25.20.

$C_9H_{18}O_4S_2$ . Calculated %: S 25.40.

#### VI. Di-( $\gamma$ -cyano-propyl)-disulfone-dimethylmethane

Into a triple-necked flask, fitted with a mechanical stirrer and a reflux condenser, were introduced 12 g of potassium cyanide and 13 ml of water. To the solution obtained were added 27 g of alcohol. Upon heating, a homogeneous solution was formed, after which 25 g of di-( $\gamma$ -chloropropyl)-disulfone-dimethylmethane was added. The solution was brought to boiling, which was continued for 12 hours. The temperature of the bath was kept at 85-90°. As a result, an oily, dark-colored liquid was obtained which was separated from the water-alcohol layer. The oil was shaken 4-5 times with ether, a fresh portion of ether being used for each shaking. As a result of this treatment with ether, the oil crystallized out. The crystallized product was boiled with double its weight of 95% alcohol for 30 minutes in the presence of 3 g of activated carbon. White needles were obtained, m.p. 76-77°; the yield of the pure compound was 16.5 g, which is 70% of the theoretical yield. The compound, similar to the 'dichloride', is almost insoluble in water; easily soluble in dichloroethane, chloroform, benzene, toluene; poorly soluble in cold alcohol, easily in hot.

Found %: S 21.22.

$C_{11}H_{18}O_4N_2S_2$ . Calculated %: S 20.91.

#### VII. $\gamma,\gamma'$ -Di-(carboxy-propyl)-disulfone-dimethylmethane

Into a 200 ml flask, heated on an oil bath, were added a previously prepared mixture of 34 ml of concentrated sulfuric acid, 34 ml of acetic acid and 34 ml of water. To this mixture were then added 17 g of 'dinitrile'. The mixture was brought to boiling. In order to maintain boiling, the temperature of the bath was held at 160° at the beginning of the reaction, then gradually raised to 200°. The boiling was maintained for one hour. The reaction mixture was allowed to cool to 30°, after which it was poured into 1 l. of cold water. The product separated as needles, which were filtered from the acidic liquid. The precipitate obtained was dissolved in a 5% solution of sodium hydroxide; the solution was filtered from the impurities insoluble in alkali; the filtrate was acidified with 10% hydrochloric acid to an acid reaction. The crystals which then separated were again filtered. The precipitate was then boiled with three times its volume of water and 2 g of activated carbon for 30 minutes. 13 g of the dicarbonic acid was obtained. The yield was 68.5% of the theoretical;



m.p. 144-145°. The acid is difficultly soluble in cold water, easily in hot; easily soluble in cold alcohol; poorly soluble in cold benzene, chloroform, easily in hot benzene and chloroform. It gives a blue coloration with ferric chloride.

Found %: S 18.79, 18.92.  
 $C_{11}H_{20}O_8S_2$ . Calculated %: S 18.60.

#### VIII. $\gamma, \gamma'$ -Di-(carbo-methoxy-propyl)-disulfone-dimethylmethane

To 20 g of methanol were added, with external cooling, first 2 g of sulfuric acid and then 3 g of the dicarbonic acid obtained above. This mixture was boiled for 15 hours, after which the reaction mixture was poured into cold water. The precipitate was then filtered, washed with a 5% solution of soda to a weakly alkaline reaction and then washed with water to a neutral reaction. The product obtained is of a light-cream color and melts at 93-94°. After recrystallization from hot water in the presence of activated carbon, the m.p. is 97-98°. 2.5 g of the pure compound was obtained, or 77% of the theoretical yield. The compound is poorly soluble in cold water, easily in hot, soluble in alcohol.

Found %: S 17.01, 17.04.  
 $C_{13}H_{24}O_8S_2$ . Calculated %: S 17.21.

#### IX. Di-(chloro-propyl-disulfone)-pentamethylenemethane

Obtained analogously from cyclohexanone and  $\gamma$ -chloropropylthiosulfate. Sp. gr. of the mercaptol at 18° is 1.135. The melting point of the di-( $\gamma$ -chloropropyl)-disulfone-pentamethylenemethane obtained is 68-70°. Insoluble in cold water, poorly in hot; poorly soluble in cold alcohol, easily in hot; easily soluble in ether, acetone, benzene, toluene, chloroform and dichloroethane.

Found %: S 17.85, 17.93.  
 $C_{12}H_{22}O_4S_2Cl_2$ . Calculated %: S 17.53.

#### X. 1,2-Cyclobutylene-dimethylene-disulfone-pentamethylenemethane

Obtained analogously to 1,2-cyclobutylene-dimethylene-disulfone-dimethylmethane by the action of an aqueous solution of potassium hydroxide on di-( $\gamma$ -chloropropyl)-disulfone-pentamethylene-dimethylmethane. M.p. 154.5°; yield, 85% of theoretical. Soluble in boiling water 1:500.

Found %: S 22.07.  
 $C_{12}H_{20}O_4S_2$ . Calculated %: S 21.92.

I wish to express my gratitude to the director of the laboratory, Prof. O. Yu. Magidson, for his valued advice and instruction, of which I made use in the fulfillment of the present work.

#### SUMMARY

1. Methods for the preparation of acyclic disulfones have been worked out.
2. The preparation of ten different compounds of the above series have been described.

#### LITERATURE CITED

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## STUDY OF THE OXIDATION OF IRON SULFIDE BY OXYGEN

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The oxidation of metallic sulfides is a complex process, consisting of a whole series of intermediate reactions. Besides the fundamental reactions between sulfide and oxygen, a whole series of secondary reactions take place, such as the reactions of sulfides with  $\text{SO}_2$  or  $\text{SO}_3$ , of oxides with  $\text{SO}_3$ , etc.

V.I.Smirnov in a survey article [1], as well as in other works [2] described in detail the results of separate investigations on the transformations of copper ores and concentrates upon oxidative roasting.

N. P. Diev and U. V. Kariakin [3] conducted a whole group of investigations on the oxidation of sulfides by air enriched with oxygen, for the purpose of studying the application of oxygen in the metallurgy of non-ferrous metals. K. M. Malin [4], B. D. Miel'nik et al. studied the rate of combustion of pyrites and pyrrhotine in order to explain the kinetic mechanisms involved and to investigate the possibility of intensifying the roasting process.

An investigation of the oxidation of metallic sulfides is of interest not only for the chemical and metallurgical industries, but also to explain the cause and find the means of prevention of subterranean fires in copper pyrites deposits [5].

A series of investigations on the spontaneous combustion of pyrite ores is also concerned with this question [7].

In the present work we conducted an investigation on the oxidation of iron sulfide by oxygen under a wide range of pressures with the purpose of giving greater definition to the kinetic reactions involved and to the mechanism of the process.

### Method and Apparatus

For carrying out the kinetic experiments a vacuum system was used with the gas circulating in an enclosed space, in which was measured the decrease in pressure resulting from the condensation of the gaseous products of the reaction in a liquid oxygen trap. The rate of oxidation of the iron sulfide was calculated from the amount of oxygen used up in the reaction in unit time. At low oxygen pressures ignition of the sulfide did not occur even at high temperatures, therefore an accurate temperature relationship with the reaction rate could not be obtained.

The diagram of the apparatus is given in Fig. 1. Into the quartz reaction tube 1, situated in a specially constructed vacuum furnace 2, described in detail in another paper, 0.5 g of the sulfide was introduced. After the apparatus was closed, it was evacuated to a high vacuum by a Langmuir pump 16, and the degasification of the sample effected. Then a Dewar vessel with liquid oxygen was placed under the trap 3, a portion of the gas from flask 24 was admitted until the

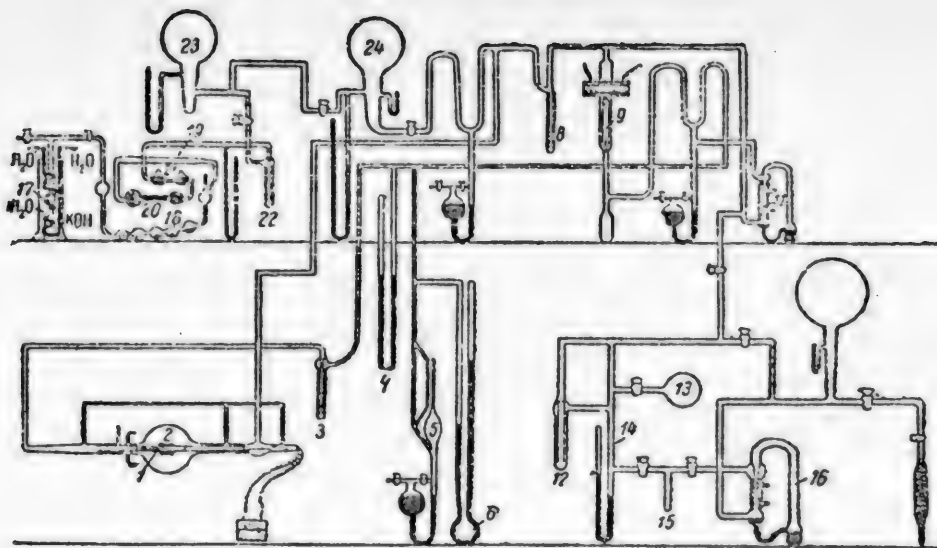


Fig. 1 Diagram of the Apparatus

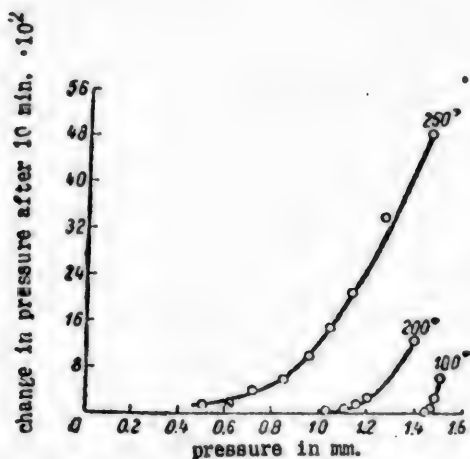


Fig. 3 Kinetics of the Oxidation of FeS, at 100-250°

O<sub>2</sub> pressure 1.5 mm.

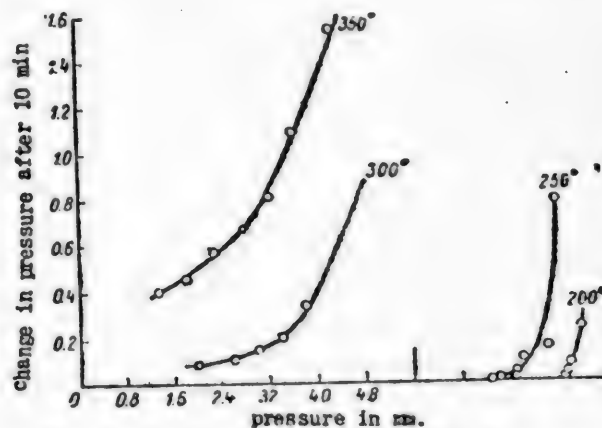


Fig. 4 Kinetics of the Oxidation of FeS at 200-250°

Initial O<sub>2</sub> pressure 8 mm.

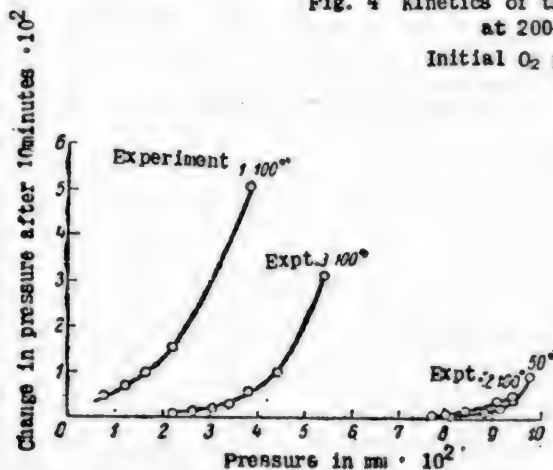


Fig. 2 Kinetics of the Oxidation of FeS at 50-100°  
Initial O<sub>2</sub> pressure 0.1 mm.

necessary pressure required for conducting the experiment was obtained, and the circulation of the gas was started, either by the Langmuir pump 11 for pressures less than 10 mm, or by the glass piston pump 9 for greater pressures. The course of the reaction was followed by the change in pressure in relationship to the initial pressure after definite intervals of time by manometers 4,5,6. Knowing the volume of the circulating portion of the system and the amount of the solidified gases  $\text{SO}_2$  and  $\text{SO}_3$ , it was possible for us to calculate the kinetics of the process at any instant of time.

The oxygen necessary for the investigation was obtained by electrolysis of a solution of  $\text{KOH}$  17 and purified by passing through a solution of  $\text{KOH}$  18, heated platinized silica gel 19, calcium chloride 20,  $\text{P}_2\text{O}_5$  21, and finally dried in the trap 22, submerged in liquid oxygen. The pure and dry gas was collected in flasks 23 and 24.

Analysis of the gaseous products of the reaction was based on the manometric determination of their total quantity and by their subsequent separation with the aid of cooling mixtures. After the experiment the oxygen was evacuated from the apparatus,  $\text{SO}_2 + \text{SO}_3$  transferred from trap 3 to trap 12, evaporated in a small but exactly known volume and their total pressure measured. Then both gases were again frozen at the temperature of liquid oxygen in trap 12 and the temperature raised to  $-95^\circ$ . At this temperature the vapor tension of  $\text{SO}_3$  is negligibly small and  $\text{SO}_2$  was evaporated and condensed in trap 15, submerged in liquid oxygen. The separation of the gases was concluded in 20 minutes and their quantity determined by measuring the pressure in a known volume after thawing.

Analysis of the solid products of the reaction was carried out by chemical, X-ray and magnetic methods. The sulfide sulfur was determined by chemical analysis according to the method of Classen-Finkener [8], the total amount of iron and sulfate sulfur in the aqueous extract was determined by the dichromate method of Penny [9]. The X-ray analysis was carried out by the method of Debye-Sherrer, previously having taken roentgenograms of  $\text{FeS}$ ,  $\text{FeS}_2$ ,  $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{FeSO}_4$ . Magnetic analysis was used for determining the concentration of magnetite in the solid products of the reaction, i.e. in its mixtures with non-magnetic compounds of iron. The method is based on the fact that the magnetic saturation is proportional to the amount of magnetite in the mixture. The magnetic circuit consisted of an electromagnet with a strong magnetic pole, at which the magnetite was almost completely saturated. A calibrated straight line was previously drawn for the mixture  $\text{Fe}_3\text{O}_4 + \text{Fe}_2\text{O}_3$  of different percent compositions. The method permitted the magnetite content to be determined with an accuracy of up to 2%.

#### Starting Materials

The experiments were conducted with iron sulfide obtained by two methods. In the first method the iron sulfide was obtained by melting reduced iron with sulfur at  $1200^\circ$ . After cooling, the fused product was ground and brought to the composition  $\text{FeS}$  by treatment with a mixture of 90%  $\text{H}_2 + 10\% \text{H}_2\text{S}$  at  $1050^\circ$ , and cooling in a current of pure nitrogen, i.e. as recommended by U.V. Kariakin [10]. In the second method the iron sulfide was obtained by the dissociation of a pure sample of pyrites in a current of nitrogen at  $700^\circ$ .

In Table 1 are given analyses of the samples of iron sulfide used for the experiments.

Since the results of the experiments are quite analogous for both samples



of iron sulfide, subsequently: we will present only data obtained using the sulfide prepared by the first method.

TABLE 1  
Analysis of Samples of Iron Sulfide

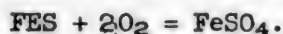
Material	S (in %)	Fe (in %)	Remarks
FeS obtained by treatment with $H_2 + H_2S$ . . . . .	36.18	63.98	Theoretical composition of FeS: S 36.48 Fe 63.52
FeS obtained by the dissociation of pyrites . . .	37.08	63.72	

#### Experimental Results

The oxidation of a clean surface of iron sulfide by dry oxygen may be observed at low temperatures and pressures. In Fig. 2 are presented experimental results at 50 and 100° and initial oxygen pressures of 0.1 mm. The rate of reaction is placed at the ordinate and is expressed by the amount of oxygen used up for the reaction, as measured by its decrease in pressure in the closed system after 10 minutes. At the abscissa is placed the average pressure corresponding to the given rate of reaction. From this diagram the extremely rapid drop of the rate of reaction during the experiment is evident. For clean surfaces of sulfide the reaction proceeds at a measurable rate even at the low temperature of 50°, but as soon as a thin layer of the solid reaction products is formed the rate begins to become negligibly small. In our experiments it was necessary to use an amount of oxygen corresponding to a decrease in pressure of the system of 0.02 mm at 50° (or  $3 \cdot 10^{-5}$  g  $O_2$  for 0.5 g FeS), 0.1 mm at 100° and 0.3 mm at 150°, or the reaction would take place extremely slowly. For the indicated amount of oxygen an almost monomolecular layer of the reaction product may be formed on the surface of the sulfide at 50° (the area of the surface of 1 g of FeS is about  $0.1M^2$ ). At higher temperatures (100-150°) the product of the reaction,  $FeSO_4$ , decomposes to FeS as fine crystals with a width 5-15 times larger than the crystal lattice constant.

The results of three successive experiments at 100° are given in Fig. 2. The first experiment took place comparatively rapidly, but during the experiment an inhibiting layer of reaction product was formed, and therefore the second experiment proceeded extremely slowly. Before the third experiment the sample was heated at 600° in vacuo, whereupon the iron sulfate formed in the first two experiments dissociated and at the surface of the sulfide a more porous and therefore less inhibiting layer of iron oxides remained, and as a result, the third experiment at 100° proceeded with considerable speed.

The oxidation of iron sulfide at the low temperatures of 50-150° takes place without the formation of  $SO_2$  or  $SO_3$ , since none of these gases were found in the trap cooled with liquid oxygen. Therefore all the oxygen used for the reaction is combined with the sulfide with the formation of a surface chemical compound or  $FeSO_4$  according to the reaction:



The iron sulfate isolates the underlying layer from contact with oxygen, and the rate of the reaction diminishes sharply. Increasing the temperature to 600° causes decomposition of the sulfate, and the iron oxide formed as a result of

the dissociation of the sulfate has a decreased inhibitory influence on the reaction because of the greater porosity, which is confirmed by experiment No. 3, shown in Fig. 2.

Quite analogous results were obtained at higher oxygen pressures. Experimental results for initial oxygen pressures of 1.5 mm and 8 mm are presented in Figs. 3 and 4. The oxidation reaction practically ceases upon use of an amount of oxygen corresponding to a decrease in pressure in the system of 0.1 mm at 100°, 0.5 mm at 200°, 1.0 mm at 250°, which corresponds to from 0.04% to 0.40% of the complete conversion of sulfide to sulfate.

Although a considerable decrease in the reaction rate during the reaction is observed at 300° and especially at 350°, the reaction still proceeds at a measurable rate, evidently because of the marked dissociation of the sulfate and consequently the gradual decomposition of the inhibitory layer. At still higher temperatures the iron sulfate dissociates with greater speed, and its inhibitory influence becomes still weaker. Collecting the gaseous products of the reaction confirmed the above, that is, beginning with 300°, SO<sub>2</sub> and SO<sub>3</sub>, which are products of the dissociation of iron sulfate, appear in the gaseous phase.

Results of the analysis of the solid phases of the products of incomplete oxidation, obtained by roentgenographic, magnetic and chemical means, indicated that at oxidation temperatures of 350-400° there is contained up to 12% and higher of iron sulfate. At oxidation temperatures over 450° there are always found Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> in the products of the reaction, the ratio of the percent composition Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> increasing as the sulfur is burnt out, which is evident from Table 2 showing the phase composition of the reaction products for several experiments.

TABLE 2  
Phase Composition of the Reaction Products

Exp. No.	Temperature of the experiment	Oxygen pressure in mm	Composition of the solid phase, %		
			FeS	Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub>
1	450°	100	69.1	24.9	5.0
2	800	50	66.6	23.7	9.7
3	500	50	59.7	22.9	17.4
4	600	100	36.0	20.1	43.9
5	500	400	0.2	8.1	92.0

#### SUMMARY

Oxidation of clean surfaces of iron sulfide by dry oxygen takes place at low temperatures (to 250°) and pressures with the formation of superficial chemical compounds or iron sulfate without the separation of SO<sub>2</sub> or SO<sub>3</sub>. The rate of reaction drops sharply upon formation of reaction products, becoming practically equal to zero for a very thin layer of iron sulfate with a crystal width several times that of the crystal lattice constant. Decomposing the sulfate layer by roasting at 600° or at higher temperatures reduces the reactive capability of iron sulfide towards oxidation at low temperatures, since the iron oxides obtained as a result of the dissociation of the sulfate form a more porous layer, which does not possess such a strong inhibitory influence on the reaction as does iron sulfate.

At oxidation temperatures of 350-450° a marked dissociation of iron

sulfate occurs, and the layer of the latter acquires sufficient porosity to admit oxygen to the reaction locale; therefore the oxidation of sulfide at the above temperatures may be carried out almost to completion with the formation of iron sulfate mixed with iron oxides as products of the reaction.

At temperatures above  $450^{\circ}$  the iron sulfate dissociates with considerable rapidity, and its inhibitory influence on the oxidation of iron sulfide becomes insignificant. At the higher temperatures, another phenomenon appears - caking of the solid reaction products, limiting the kinetics of the process. The products of the reaction consist of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ; the ratio of the percent composition  $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  increases upon burning off the sulfur.

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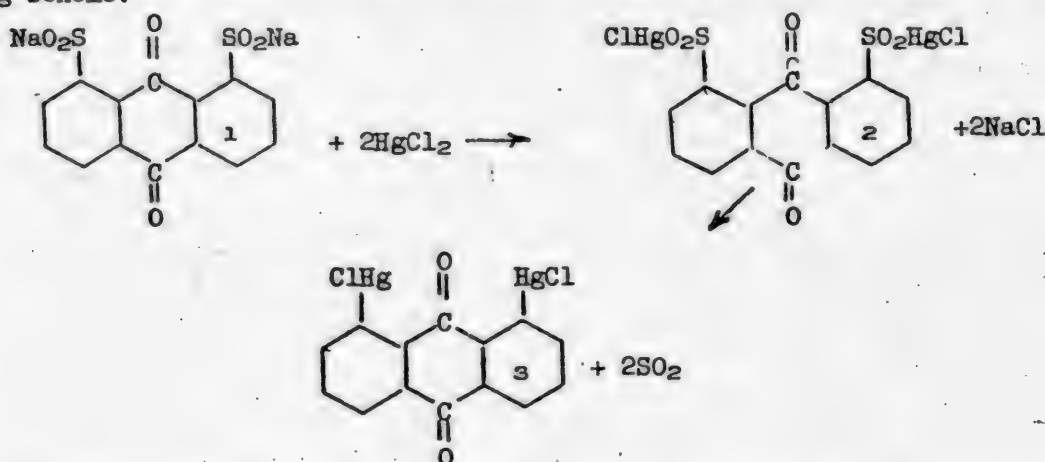
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# INVESTIGATION OF THE ANTHRAQUINONE SERIES

## XVI. ON 1,8-MERCURY-CONTAINING UNSYMMETRICAL COMPOUNDS OF ANTHRAQUINONE\*

V. V. Kozlov and D. D. Smolin

In synthesizing and studying the properties of derivatives of 1,5-anthraquinonyl-mercury, described in a previous paper, we undertook the preparation of mercury-containing compounds of anthraquinone for the 1,8-substitutions. For this purpose, we employed a method [1] which may be expressed by the following scheme:

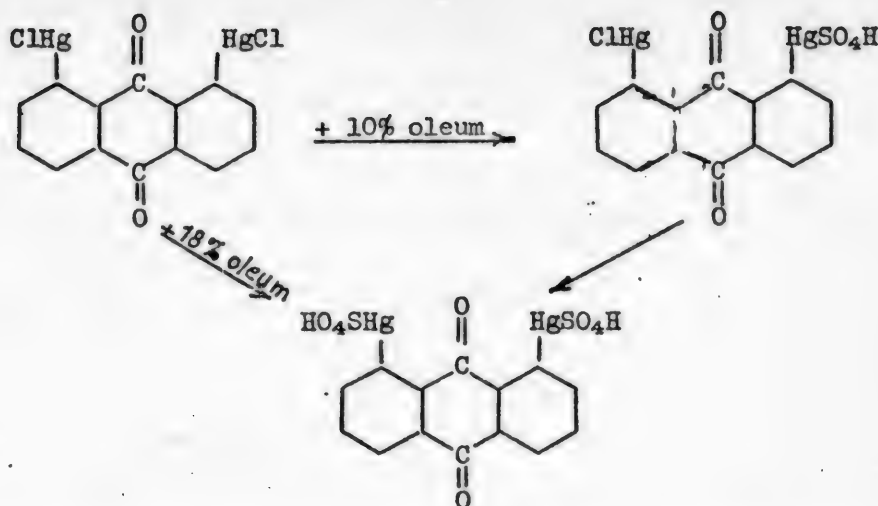


The realization of these transformations was assured by using as a starting material the 1,8-disulfonic acid of anthraquinone which was first obtained by us [2].

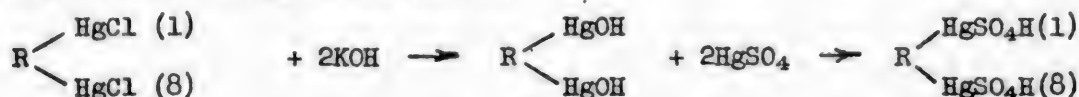
By the action of an easily soluble salt of 1,8-disulfonic acid [1] with mercuric chloride, the insoluble di-mercury salt is not separated, in contradistinction to the 1,5-isomer [2]. Continuous boiling of the solution leads to the evolution of  $\text{SO}_2$  and the formation of an amorphous precipitate, corresponding to the chloride of 1,8-anthraquinonyl mercury [3]. Yield is 85%, based on the original disulfonic acid. Substance is a bright yellow powder, virtually insoluble in common organic solvents, and difficultly freed from impurities, including sulfur, by extraction with carbon disulfide and reprecipitation by water from a sulfuric acid solution. The substance is easily soluble in the cold in weak oleum with the formation of a bright yellow-orange color, and in concentrated sulfuric acid at 40-50°. It decomposes, without melting, over 300°. The conversions, which we presented previously, of  $\alpha$ -anthraquinonyl mercury chloride [4] and of 1,5-anthraquinonyl mercury [2] to 1,8-anthraquinonyl-mercury sulfate by the action of 10-18% oleum in the cold, also take place smoothly with 1,8-anthraquinonyl-mercury, and more easily than for the 1,5-isomer, according to the scheme:

\* See report XV, YCOX, 19 319 (1949).

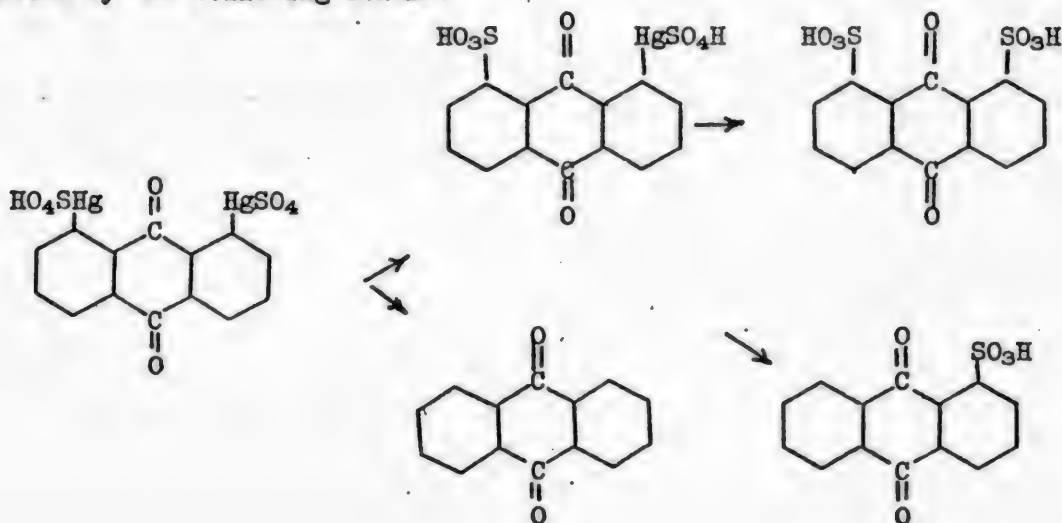




The 1,8-anthraquinonyl-mercury sulfate so obtained was identical with the substance obtained by the standard method for converting 1,8-anthraquinonyl-mercury chloride according to the scheme:

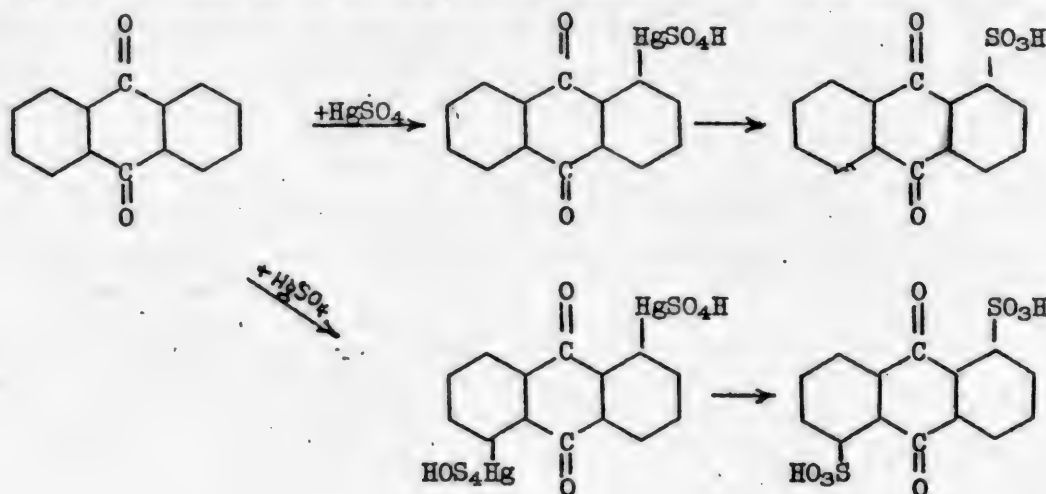


As with the 1,5-isomer, oleum of a high concentration (30-40%) in the cold and more quickly upon heating, results in a decomposition of the mercury compound with the formation of anthraquinone disulfonic acid. Upon treatment of 1,8-anthraquinonyl-mercury sulfate for 30 minutes with 150% of the theoretical quantity required of 10% oleum at 140°, the following have been stated to be formed: 1,8-anthraquinonedisulfonic acid, 20% of the theoretical;  $\alpha$ -anthraquinone sulfonic acid, 19.5% of the theoretical; anthraquinone - traces; 1-sulfo-8-anthraquinonyl mercury sulfate - 11% and unchanged 1,8-anthraquinonyl-mercury sulfate to 48.6%. Thus, the transformation of 1,8-anthraquinonyl-mercury sulfate may be expressed by the following scheme:



Sulfonation with 150% of theoretically required 25% oleum for 1.5 hours at 140° leads to the formation of 1,8-anthraquinone disulfonic acid, 76% of the theoretical;  $\alpha$ -anthraquinone sulfonic acid - 4.5%; 1,5-anthraquinone disulfonic acid - 8.0%; anthraquinone - 6.5%, and the oxysulfonic acid - traces (coloration with NaOH).

Thus, in the general scheme for the transformation of 1,5- and 1,8-anthraquinonyl-mercury sulfate, the behavior of the latter isomer leads to a larger number of different compounds as a result of the greater instability of the mercury compound. The 1,5-disulfonic acid, as well as the  $\alpha$ -sulfonic acid, is prepared by the sulfonation of anthraquinone, according to the scheme:



## EXPERIMENTAL

### 1. Preparation of 1,8-Anthraquinonyl-mercury Chloride

1.68 g of the sodium salt of 1,8-anthraquinone disulfonic acid [2] (0.005 M) was dissolved in 80 ml of 0.1 N sodium hydroxide and the result added to a solution of 5 g of mercuric chloride in 20 ml of boiling water. Upon pouring the solutions only a slight cloudiness is first formed, and then upon heating to boiling, an abundant amorphous precipitate begins to separate. A 0.1 N solution of NaOH was then added to the reaction mixture to the disappearance of an acid reaction to Congo red paper and the boiling was continued for 3 hours. When the heating was completed the precipitate was filtered off, washed with hot water, boiling acetic acid, alcohol, and dried. Weight was 2.87 g.

Analysis for Mercury (Koshkin [3]):

0.1817 g substance; after decomposition with sulfuric acid, it was dissolved in 100 ml of water. For the titration of 1 ml of the solution, 0.89 ml of 0.01 N KI solution was used ( $T_{\text{KI}} = 0.001178 \text{ g Hg.}$ ).

Found %: Hg 58.20.

Calculated %: Hg 59.08.

Analysis for Chlorine:

0.1998 g substance: 0.0872 g AgCl.

Found %: Cl 10.83

Calculated %: 10.48.

### Analysis for C and H

0.2112 g substance: 0.1936 g CO<sub>2</sub>; 0.0180 g H<sub>2</sub>O.

Found %: C 25.01; H 0.99.

C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>Hg<sub>2</sub>Cl<sub>2</sub>. Calculated %: C 24.81; H 0.88.

### 2. Preparation of 1,8-Anthraquinonyl Mercury Hydroxide

1.0 g of 1,8-anthraquinonyl-mercury chloride was suspended in a solution of 15 g of KOH in 60 ml of dry methyl alcohol, after which it was heated in a flask with a reflux condenser over a boiling water bath for 6 hours. After heating the alcoholic solution took on a reddish-brown color and the suspended substance undergoes some change. The precipitate was converted from a bright-yellow to greenish-gray powder, insoluble in solvents. The product does not contain chlorine, but contains mercury. The yield is 0.81 g, or 86.16% of the theoretical, based on anthraquinone-bis-hydroxy-mercury.

### 3. Preparation of 1,8-Anthraquinonyl Mercury Sulfate

1) 0.5 g of 1,8-anthraquinonyl mercury hydroxide was finely ground and added, with mixing, to 10 ml of sulfuric acid (sp. gr. 1.84) cooled to 0°. The substance quickly dissolves with a reddish-brown color. The solution, which is completely transparent and free from insoluble particles, is carefully diluted, dropwise, with 3 times its quantity of water. The precipitate which separates is filtered off, washed with water, alcohol and dried in a vacuum-desiccator. The yield is 0.6 g, or 88.1% of the theoretical, based on 1,8-anthraquinonyl-mercury sulfate. The substance, like the 1,5-isomer, is practically insoluble in organic solvents, in sulfuric acid, but dissolves comparatively easily, with a dark brown coloration, in weak oleum. The substance does not melt. When the filtrate was further diluted with water, flakes were separated which were shown to be anthraquinone with a m.p. of 280.5° and were present in somewhat greater quantity than we noted for the 1,5-isomer.

Analysis of 1,8-anthraquinonyl-mercury sulfate for mercury:

0.1398 g substance: 100 ml water. For titrating 1 ml, 0.55 ml of 0.01 N KI solution ( $T_{KI} = 0.001175$  g Hg) was used.

Found %: Hg 50.18.

Analysis for sulfur:

0.3008 g substance: 0.1729 g BaSO<sub>4</sub>.

Found %: S 7.88.

C<sub>14</sub>O<sub>2</sub>H<sub>8</sub>(HgSO<sub>4</sub>H)<sub>2</sub>. Calculated %: Hg 50.00; S 8.00.

2) 0.1 g of 1,8-anthraquinonyl-mercury chloride was dissolved in 25 g of 10% oleum at 30-35° for 6 hours. After pouring the filtered solution, so obtained, over ice, a dark-gray substance separated, weighing 0.99 g or 77.31% of the theoretical, based on the anthraquinonyl-mercury sulfate. From its properties, the substance is analogous to that obtained above.

Analysis for mercury:

0.512 g substance: 100 ml water. For titrating 1 ml, 0.62 ml of 0.01 N KI solution was used ( $T_{KI} = 0.001172$  g Hg.).

Found %: Hg 49.74.

#### Analysis for sulfur

0.2416 g substance: 0.1374 g BaSO<sub>4</sub>

Found %: S 7.81.

#### Analysis for C and H

0.3416 g substance: 0.2599 g CO<sub>2</sub>; 0.0306 g H<sub>2</sub>O.

Found %: C 20.77; H 0.99.

C<sub>14</sub>O<sub>2</sub>H<sub>6</sub>(HgSO<sub>4</sub>H)<sub>2</sub>. Calculated %: Hg 50.00; S 8.00; C 21.00; H 1.00.

3) 1.0 g of 1,8-anthraquinonyl-mercury chloride was dissolved in 20 g of 18% oleum in the cold for 6 hours. The product which separated upon pouring over ice was washed with cold and hot water, then heated with acetic acid, then again with water. The yield was 0.95 g or 73.17% of the theoretical, based on the anthraquinonyl-mercury sulfate.

#### Analysis for mercury:

0.1717 g substance: 100 ml water. For titrating 1 ml, 0.69 ml of 0.01 N KI solution ( $T_{KI} = 0.001172$  g Hg) was used.

Found %: Hg 49.88.

#### Analysis for sulfur:

0.2108 g substance: 0.1245 g BaSO<sub>4</sub>.

Found %: S 7.89.

C<sub>14</sub>O<sub>2</sub>H<sub>6</sub>(HgSO<sub>4</sub>H)<sub>2</sub>. Calculated %: Hg 50.00; S 8.00.

#### 4. Sulfonation of 1,8-Anthraquinonyl-mercury Sulfate

1) 4.0 g of the substance was sulfonated with 12 g of 10% oleum at 140° for 30 minutes. It has been stated that the 1,8-disulfonic acid and the  $\alpha$ -sulfonic acid of anthraquinone are present in the aqueous solution. The latter separated with chrysoidin (1% solution) as a difficultly soluble salt. From the mother liquor, the dipotassium salt of the 1,8-disulfonic acid was salted out. The yield of the  $\alpha$ -sulfonic acid salt of anthraquinone was 0.29 g; chloroanthraquinone obtained from it melts at 159.5° and does not depress the melting point upon admixture with pure  $\alpha$ -chloroanthraquinone. The insoluble residue from the sulfonation weight 2.32 g, was shown to contain mercury and sulfur and, in contrast with the original substance, is a compound extractable by acetic acid. The residue, insoluble in acetic acid, (about 2 g), is the unchanged 1,8-anthraquinonyl-mercury sulfate. Upon diluting the acetic acid solution with water, 0.3 g of a brownish product separates, which blackens upon heating to about 325°.

#### Analysis

0.0982 g substance: 100 ml water; for 1 ml, 0.3 ml of 0.01 N KI solution was used ( $T_{KI} = 0.001172$  g Hg).

0.1101 g substance: 0.0876 g BaSO<sub>4</sub>.

0.1002 g substance: 0.0967 g CO<sub>2</sub>; 0.0117 g H<sub>2</sub>O.

Found %: Hg 34.26; C 29.00; S 11.10 H 1.25.

Substance taken for 1-sulfo-8-anthraquinonyl-mercury sulfate:

C<sub>14</sub>H<sub>6</sub>O<sub>2</sub>HgSO<sub>4</sub>H·SO<sub>3</sub>H. Calculated %: Hg 34.24; S 10.95; C 28.36; H 1.35.

2) 4.0 g of the substance was sulfonated with 4.8 g of 25% oleum at 140° for 1.5 hours. No mercury was found in the insoluble residue, weight 0.07 g, but traces of the hydroxy compound were present. Upon sublimation pure anthraquinone



was obtained. In the acid mother-liquor, the presence of the following was established by qualitative reactions: 1,8-disulfonic acid, 1,5-disulfonic acid, and the  $\alpha$ -sulfonic acid of anthraquinone. The latter was separated from the disulfonic acids by precipitating it with chrysoidin. The dipotassium salt of the mixture of disulfonic acids was separated from the second mother liquor, and weighed 1.9 g. It was converted to a chloroanthraquinone with a m.p. of 196°, which corresponds to a 10% content of 1,5- and a 90% content of 1,8-anthraquinone disulfonic acid. Thus, the following was determined in the sulfo-mixture:  $\alpha$ -sulfonic acid 0.08 g; K-salt of 1,5-disulfonic 0.19 g; K-salt of 1,8-disulfonic acid 1.71 g.

#### SUMMARY

1. 1,8-Anthraquinonyl-mercury sulfate and several of its derivatives have been synthesized.

2. It was established that by the action of oleum on the chloride or sulfate of 1,8-anthraquinonyl mercury, the 1,8-disulfonic acid of anthraquinone is formed as the fundamental reaction product. Its formation proceeds with greater rapidity and at a lower temperature and oleum concentration than the formation of sulfonic acids by disulfonation of anthraquinone with mercury.

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\* C. B. English translation page 717 (April, 1949).

## ALKALOIDS OF DELPHINIUM BITERNATUM

### II. ALKALOIDS OF THE FAMILY RANUNCULACEAE

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The different forms of Delphinium have long been used in medicine as medicinal plants for the treatment of wounds, epilepsy, dropsy, eye disease, from which the name 'zhivokost' is derived. Several of them have found application as insecticidal and pediculicidal agents (seed of D. consolida, oil of D. staphisagria). By their toxic action, the alkaloids of Delphinium are very closely related to the alkaloids of aconites. There are also data in the literature [1] on the fact that several Delphinium alkaloids, similar to curare, cause paralysis of the terminal motor nerves.

The extreme toxicity of plants of the Delphinium genus has long attracted the attention of investigators. The base delphinine, separated by Brandes and Lassen [2] in 1819 from D. staphisagria, was one of the first discovered alkaloids. Many investigators undertook further studies of the Delphinium alkaloids, and at the present time 22 new alkaloids have been separated and described from nine different genera of Delphinia (D. staphisagria [3,4,5,6,7], D. scopulorum [1], D. consolida [8,9], D. ajacis [10,11,12], D. elatum [5,13], D. occidentale [14], D. brownii [15], D. sp. [16], D. confusum [17]).

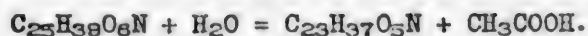
However, notwithstanding these considerable investigations, our knowledge of the chemical nature of the Delphinium alkaloids is to date very limited. In view of the complexity of the chemical structure of these high molecular weight compounds, as well as the experimental difficulties encountered in their purification and characterization, investigators have limited themselves primarily to separating the alkaloids, and therefore the various authors often differ among themselves even on the relative element formulas of the bases. To indicate the difficulties of investigating these alkaloids it is sufficient to say that the final gross-formula and nature of the substituted groups of the delphinine  $C_{34}H_{47}O_9N$ , the most widely studied of all the delphinium bases described in the literature, had been established by Jacobs and Graig [7] only in 1939, over one hundred years from the time of its discovery.

The most interesting and important of the enumerated investigations are the discoveries of recent years. The morphological similarity of the Delphinium and Aconitum genera, the similarity of their pharmacological action, and also the comparative data on the structure of the delphinium and aconite alkaloids, have for some time been shown to have an obvious connection, but facts confirming the resemblance of their chemical structure have until now not been presented.

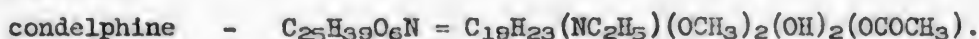
In 1942 Rabinovich and Konovalova [17], studying the Central Asiatic plant D. confusum, separated a new alkaloid from it, Condolphine  $C_{25}H_{39}O_6N$ . By washing the latter with alcoholic alkali the authors obtained the amino

\* Literal translation - "living bone".

alcohol, completely identical with isotalatizidine - an alkaloid earlier separated by Knovaalova and Orekhov [18] from *Aconitum talassicum*:



It is quite easy to note the resemblance of the chemical structures of condelphine and isotalatizidine, if their formulas are expanded in the following fashion:



Thus, the base - condelphine from *D. confusum* - was shown to be acetyliso-talatizidine, and for the first time indicated the direct connection between the alkaloids of the two close genera of the family Ranunculaceae - Delphinium and Aconitum.

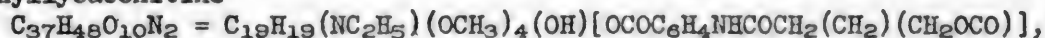
As a result of this, Goodson [13] in 1943, continuing the investigation of of *D. elatum* initiated by Keller [6], isolated three new bases - delpheline  $C_{25}H_{39}O_6N$ ; delatine  $C_{19}H_{25}O_3N \cdot H_2O$ ; methyllycaconitine  $C_{37}H_{48}O_{10}N_2$ . Upon hydrolyzing the latter alkaloid, Goodson obtained methylsuccinic acid, anthranilic acid and the amino acid of lycoctonine  $C_{25}H_{39}O_7N \cdot H_2O$ , which is the final hydrolysis product of lycaconitine  $C_{36}H_{48}O_{10}N_2$ , and is an amorphous base separated by Schulze and Bierline [19] from the roots of the Swedish type of Aconitum lycoctonum. It was shown by Goodson that the alkaloid ajacine from *D. ajacis* [10,11] and the amorphous base from *D. brownii*, described by Manske [15], gave the same lycoctonine as a final hydrolysis product.

The formulas of the above-described related alkaloids may be partially developed in the following fashion:

lycaconitine



methyllycaconitine



ajacine



lycoctonine



Consequently all three alkaloids are derivatives of one and the same compound of lycoctonine, and the difference between them lies only in the fact that the esterified amino alcohol of anthranilic acid is an amide of succinic acid for lycaconitine and an amide of methylsuccinic and acetic acids for the delphinium alkaloids.

Botanists have described 81 species of Delphinium [20] on the territory of the Soviet Union, of which 40 were found in Central Asia. With the exception of two species [16,17], the native flora Delphinia have not been studied. To establish the nature of their alkaloid contents and the possibility of their practical application, we began work on a chemical investigation of different species of Delphinium growing in Uzbekistan and the adjacent Middle Asiatic republics. In the present paper we will present the first results obtained in the investigation of the species Delphinium biternatum.

Delphinium biternatum Huth. (doubly ternate larkspur) grows in mountainous regions at a height of 1500 - 2000 meters and belongs to a species which is

relatively rare and difficultly accessible for collection. As the material for our study, we used the above-ground portion and the roots of the plant, collected by an expedition of our institute, headed by E.E. Korotkova, to the northwest slopes of the Kuraminski chain in the valley of the Lyaskarak river (territory of Tashkent) in the summer of 1946. The plant was collected at the end of May, when it had just begun to form buds.

The separation of the alkaloids was accomplished by the usual method - extraction with dichloroethane. The content of alkaloids in the plant proved to be quite considerable, a somewhat greater quantity being found in the roots than in the above-ground portion (0.69% and 0.62% respectively of the dry weight of the plant). Fractionation by means of different solubilities in light benzine, ether and chloroform showed that it was possible to separate the mixture of bases into three parts. The portion soluble in benzine, a thick, light yellow mass, was almost completely converted to the crystalline perchlorate, and by decomposing the latter the free base was obtained. Upon concentrating the ether fraction, small crystals of another base separated. The alkaloid mixture remaining in the ether mother-liquor and the chloroform solution was not studied in detail because of insufficient material.

The first base, which we call delphatine, is the major portion of the alkaloid mixture. Its contents in the roots as well as in the above-ground portions are equal - 0.43% of the weight of the plant. The pure substance crystallizes from a mixture of petroleum and sulfuric ether in large, rhombic prisms, m.p. 101-106°,  $[\alpha]_D^{25} + 38.5^\circ$  (in chloroform). The insufficiently sharp melting point of the alkaloid prompted us to attempt to purify it by obtaining the perchlorate a second time and again separating the free base. However, this method did not yield the expected results. The base, which was repeatedly separated from the perchlorate, invariably had a low melting point, crystallized with difficulty, and darkened quickly in air, especially in solutions, its specific rotation being then lowered. It is possible that as a result of the continued 'rough' treatment a partial isomerization of the base took place. The delphatine perchlorate, in contradistinction to the alkaloid itself, is fully stable.

Besides the perchlorate, we also obtained a crystalline iodomethylate with a good yield. The data on the elementary analysis of the alkaloid, the complete analysis of its perchlorate, the determination of iodine in the iodomethylate and finally the determination of the molecular weight by titration, all giving analogous results, permits the postulation that delphatine is a separate substance with an empirical formula  $C_{27}H_{45}O_7N$ .

The presence of five methoxyl groups and an alkylimide group was established in delphatine by the method of Vibok. Upon heating with alcoholic alkali the alkaloid is converted to a quite stable form, which indicates the absence of groups capable of esterification. Two free hydroxyl groups were found in delphatine by the Tserevitinov - Chugaeva Reaction. Correspondingly, the presence of three active hydrogen atoms was established in the perchlorate of the base.

The acetylation of delphatine under the conditions used for the aconite alkaloids was accomplished with great difficulty. Upon acetylation of the alkaloid with acetyl chloride in a sealed tube, a complex mixture of bases was obtained, which could be separated only by the solubility of their perchlorates. From the soluble portion of the perchlorates a small quantity of an amorphous base was obtained, which by the determination of its acyl group proved to be the monoacetyl derivative of delphatine, in which one hydroxyl group still remained free. By the saponification of this substance, the original alkaloid was obtained again.

Having thus explained the nature of the substituent groups of the new base

\* Delphatine is a rather strong base, its solutions giving a definite alkaline reaction to litmus. Delphatine perchlorate is decomposed with concentrated ammonium hydroxide only with heating, and upon cooling the solution of the base reprecipitates as the perchlorate. In a dilute solution of sulfuric acid, delphatine acts like an unsaturated compound and is not decolorized with permanganate.



and assuming that its nitrogen, as in several other delphine alkaloids (condelphine [17], delphine [21], etc.), is connected with the ethyl group, we may partially expand the formula of delphatine in the following fashion:



If now, in this formula, we hypothetically substitute hydrogen for all seven substituent groups ( $\text{C}_2\text{H}_5$ ,  $\text{OCH}_3$ ,  $\text{OH}$ ), it results in the expression  $\text{C}_{20}\text{H}_{30}\text{N}$  or  $\text{C}_{20}\text{H}_{31}\text{N}$ .

The compound  $\text{C}_{20}\text{H}_{31}\text{N}$  is the basic nucleus of several aconite alkaloids [22] - atisine, lucidusculine, cobusine. The Delphinium alkaloids - delphinine and delphamine [16] - also contain this hypothetical nucleus as their base. To these is evidently joined the new alkaloid delphatine which we separated.

It must be noted however that delphatine, as distinguished from the others, contains five methoxyl groups. The maximum number of the latter in the delphine and aconitine bases described to date usually does not exceed four (aconitine, pseudoaconitine, delphinine and others). Delphatine is the first base with such a large number of methoxyl groups.

We obtained a total of 1.3 g of the second alkaloid, which we called delbine. Its content in the roots is only 0.034% of the entire plant, and still less in the above-ground portion - 0.020%. From a mixture of ether and alcohol, delbine crystallizes in beautiful silky threads with one molecule of water (m.p. 116-118°). Upon drying in a vacuum the base loses its water of crystallization and then melts at 158°,  $[\alpha]_D^{25} + 33.9^\circ$  (in chloroform). The elementary analysis of the alkaloid results in the empirical formula  $\text{C}_{24}\text{H}_{39}\text{O}_7\text{N} \cdot \text{H}_2\text{O}$ , which however, in view of the limited amount of material we had, cannot be considered to be finally established.

We are continuing work on the study of alkaloids of species of Delphinium.

#### EXPERIMENTAL

##### Separation and Distribution of Total Alkaloid

2.9 kg. of the dried and finely ground roots of Delphinium biternatum were moistened with 3 liters of a 5% aqueous solution of ammonia, placed in a percolator, and after an hour, 10 liters of dichloroethane was added. Every two days the dichloroethane extract was poured off, treated repeatedly first with 10% and then with 5% solution of sulfuric acid and again poured into the percolator. The extraction was conducted five times. The acid solutions, totalling 1.5 liters, were filtered, made alkaline in the cold with a 25% solution of ammonium hydroxide and extracted several times with a light benzine fraction (b.p. 75-80°). After the extraction with benzine, the flocculent mass which precipitated in the ammoniacal solution was dissolved with 10% sulfuric acid, and the acid solution again made alkaline with concentrated ammonium hydroxide with continuous shaking and in the presence of ether. Finally, the solution was dried with potash, drained and extracted with chloroform.

Treatment of the Benzene Fraction. The benzene solution which was dried over ignited potash was evaporated on a water bath. The residue, a thick light-yellow oil weighing 12.4 g, was dissolved with cooling in 25 ml of a 5% solution of hydrochloric acid, filtered from the small quantity of resin which separates, and mixed with 25 ml of a solution of ammonium perchlorate saturated in the cold. After a short time the mixture congealed into a solid crystalline pulp. The impure delphatine perchlorate was filtered by suction, washed with a small quantity of water and dried in a desiccator (m.p. 212-214°). Yield 13.3 g. From the mother liquor, evaporated in air, 1.3 g of delphatine perchlorate was obtained, (m.p. 208-210°).

Treatment of the Ether Solution. The moist ether extract was evaporated to a volume of 70-80 ml (until a turbidity was formed). Upon cooling the latter, small crystals of delbine began to separate. By the addition of 2-3 drops of water the rate of crystallization was increased. The yield of the crude delbine was 0.8 g (m.p. 77-80°).

The ether mother liquor is evaporated to dryness. The residual resinous mass (4.3 g) was extracted several times with benzene, and then dissolved with warming in 40 ml of ether. Upon adding 1-1.5 ml of petroleum ether to the warm solution small, grayish crystals (0.2 g) precipitated out, proving to be delbine. After distilling the solvent the benzene extract (0.3 g) was completely converted to delphatine perchlorate.

The dark, resinous mass remaining after distillation of the chloroform (2.5 g) has, to date, not been studied in detail.

The total yield of the alkaloids was 20.0 g, which was 0.69% of the dry weight of the plant.

After breaking down the alkaloid mixture the following impure products were obtained: delphatine (calculated from the perchlorate) 12.5 g, or 62.5% of the total alkaloid; delbine 1.0 g, or 5.0% of the total alkaloid.

By a similar method, from 1.5 kg of the above-ground portion of the plant was separated 9.3 g of total alkaloid, which after further separation gave 6.4 g of delphatine (67.7% of the total) and 0.3 g of delbine (3.2% of the total).

#### 1. Delphatine

##### Separation of the Base

13.0 g of the impure delphatine perchlorate was twice recrystallized from 75 ml of alcohol. The dried crystals were ground in a mortar, placed in a small flask and mixed with 7 ml of a 25% aqueous solution of ammonium hydroxide. The contents of the flask were poured into 100 ml of ether and carefully heated on a water bath. After a short time the precipitated base was completely transferred to the ether layer. The ammoniacal solution was extracted twice more with 25 ml of ether. The combined ether extract was dried with potash and evaporated, first on a water bath, then in a dish in air. The precipitated crystalline base, weight 8.1 g, after recrystallization from a mixture of 75 ml of a low-boiling (b.p. 30-40°) petroleum ether and 5 ml sulfuric ether, melts at 101-106°.

Delphatine is very readily soluble in alcohol, acetone, ethyl acetate, chloroform, benzene, ether, fairly easily in benzene (1:5), difficultly soluble in low-boiling petroleum ether and water.

0.2262 g substance:  $\frac{1}{10} = 10.0$  in 10.0 ml chloroform

$\alpha_D + 0.87^\circ$ ,  $[\alpha]_D^{25} + 38.5^\circ$ .

0.1248 g substance: 0.3004 g CO<sub>2</sub>; 0.1036 g H<sub>2</sub>O.  
0.1515 g substance: 0.3632 g CO<sub>2</sub>; 0.1275 g H<sub>2</sub>O.  
0.1322 g substance: 0.3164 g CO<sub>2</sub>; 0.1106 g H<sub>2</sub>O.  
0.1492 g substance: 4.20 ml N<sub>2</sub> (30°, 718 mm).  
0.1244 g substance: 3.45 ml N<sub>2</sub> (30°, 718 mm).  
0.0734 g substance: 5.78 ml CH<sub>4</sub> (0°, 760 mm).  
0.1220 g substance: 10.32 ml CH<sub>4</sub> (0°, 760 mm).  
0.0222 g substance: 12.69 ml 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.  
0.0242 g substance: 14.06 ml 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.  
0.1314 g substance: 2.62 ml 0.1N HCl (methyl red).  
0.2508 g substance: 5.02 ml 0.1 N HCl (methyl red).

Found %: C 65.64, 65.38, 65.27; H 9.29, 9.41, 9.36;  
N 2.89, 2.85; OH 6.02, 6.45;  $\text{CH}_3\text{O}$  29.56, 30.04;  
M 501.5, 499.7.

$\text{C}_{27}\text{H}_{45}\text{O}_7\text{N}$ . Calculated %: C 65.41; H 9.16; N 2.83; 2 OH 6.87; 5  $\text{CH}_3\text{O}$  31.31;  
M 495.4.

#### Delphatine Perchlorate

4.0 g of the impure delphatine perchlorate was recrystallized several times from hot alcohol. After three crystallizations, the precipitated crystals and the crystals obtained by evaporating the mother liquor have the same m.p. 220-221° (with decomposition). Delphatine perchlorate is difficultly soluble in cold water, alcohol and chloroform, better - in hot water and alcohol. It crystallizes from the latter in rectangular plates, from water, in the form of prisms.

0.1778 g substance in 15 ml water;  $\frac{1}{\rho} = 10.0$ .

$\alpha_D + 0.10^\circ$   $[\alpha]_D^{22} + 8.4^\circ$ .

0.1220 g substance; 0.2438 g  $\text{CO}_2$ ; 0.0860 g  $\text{H}_2\text{O}$ .

0.1244 g substance: 0.2492 g  $\text{CO}_2$ ; 0.0876 g  $\text{H}_2\text{O}$ .

0.1726 g substance: 4.20 ml  $\text{N}_2$ ; (30°, 718 mm).

0.1686 g substance: 4.10 ml  $\text{N}_2$ ; (27°, 718 mm).

0.1492 g substance: 0.0354 g  $\text{AgCl}$ .

0.1732 g substance: 0.0420 g  $\text{AgCl}$ .

0.0242 g substance: 11.99 ml 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ .

0.0206 g substance: 10.32 ml 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ .

0.1694 g substance: 21.42 ml  $\text{CH}_4$  (0°, 760 mm).

0.1766 g substance: 18.26 ml  $\text{CH}_4$  (0°, 760 mm).

Found %: C 54.50, 54.63; H 7.89, 7.88;

N 2.47, 2.51; Cl 5.87, 6.00.

$\text{CH}_3\text{O}$  25.62, 25.90; active H 3.3, 2.8.

$\text{C}_{27}\text{H}_{45}\text{O}_7\text{N} \cdot \text{HClO}_4$ . Calculated %: C 54.38; H 7.82; N 2.35; Cl 5.95;

5  $\text{CH}_3\text{O}$  26.03; active H 3.

#### Delphatine Iodomethylate

0.5 g of delphatine was dissolved in 10 ml of methyl alcohol, mixed with 1.0 ml of methyl iodide and heated on a water bath, for 16 hours. After cooling the methanol and excess methyl iodide were evaporated in air. The residue was extracted twice with ether and then dissolved in 5 ml of acetone. Upon slowly adding ether to the acetone solution the delphatine iodomethylate precipitated after a short time as beautiful, large, conical prisms. Yield was 0.45 g. Recrystallized from 4 ml of acetone and 2 ml of ether, it had a m.p. of 197-198° (with decomposition). Very soluble in water, alcohol and acetone.

0.1275 g substance: 2.01 ml 0.1 N  $\text{AgNO}_3$ .

0.1087 g substance: 1.66 ml 0.1 N  $\text{AgNO}_3$ .

Found %: I 20.01, 19.84.

$\text{C}_{27}\text{H}_{45}\text{O}_7\text{N} \cdot \text{CH}_3\text{I}$ . Calculated %: I 19.91.

#### Hydrolysis of Delphatine

To a solution of 1.0 g of delphatine in 15 ml of methanol was added 1.0 g of potassium hydroxide. The solution was boiled for three hours on a water bath, after which the alcohol was evaporated in air. The residue was diluted with water and extracted with ether. Since the base obtained after distilling off the ether could not be crystallized, it was converted to the perchlorate. Recrystallized from alcohol, the latter melted at 219-220°. The melting point in

an admixture test was 219-220° and a comparison of the crystal form showed a complete identity of the salt obtained with delphatine perchlorate.

#### Action of Acetyl Chloride on Delphatine

2.0 g of the base was dissolved in 15 ml of acetyl chloride and allowed to stand in a sealed tube. After 10 days the tube was opened and the excess  $\text{CH}_3\text{COCl}$  distilled on a water bath. After cooling, the residue was diluted with 25 ml of water, made alkaline with concentrated ammonium hydroxide and extracted with ether. After distilling the ether to dryness, a yellow, resinous mass remained, which appeared to be a complex mixture of bases. To separate the latter, the resinous residue was dissolved in 8 ml of 5%  $\text{HCl}$  solution and mixed with a saturated solution of ammonium perchlorate. The insoluble perchlorates then settled out on the walls of the vessel and the soluble material remained in the mother liquor. The mother liquor was decanted off and alkalized with ammonium hydroxide and the separated base extracted with ether. After evaporating the ether, an amorphous powder remained, monoacetyldelphatine. Yield was 0.5 g.

Acetyldelphatine is very easily soluble in the cold in all the organic solvents with the exception of low-boiling petroleum ether.

0.1472 g substance: 28.09 ml 0.01 N  $\text{NaOH}$ .

0.1032 g substance: 19.8 ml 0.01 N  $\text{NaOH}$ .

Found %:  $(\text{CH}_3\text{CO})$  8.45, 8.25.

$\text{C}_{27}\text{H}_{44}\text{O}_6\text{N}(\text{OCOCH}_3)$ . Calculated %:  $(\text{CH}_3\text{CO})$  8.01.

#### Hydrolysis of Acetyldelphatine

0.25 g of acetyldelphatine was added to 5 ml of a 10% solution of potassium hydroxide in methyl alcohol and boiled on a water bath for 2 hours. After distilling the alcohol, the remainder was dried in a vacuum, diluted with 5 ml of water and extracted with ether. The amorphous mass remaining after evaporating off the ether was converted to the perchlorate, which after recrystallization from alcohol, melted at 220° and gave no depression in melting point with delphatine perchlorate.

#### 2. Delbine

1.0 g of the crude delbine was first recrystallized from a mixture of 10 ml of alcohol + 30 ml of water, and then with 5 ml of alcohol and 40 ml of ether. Delbine crystallized from the latter mixture in beautiful, silky threads with one molecule of water (m.p. 116-118°). Upon drying in vacuo the base lost the water of crystallization and then melted at 158° (with decomposition). In air the alkaloid again absorbs the water of hydration.

Delbine is very easily soluble in alcohol, chloroform, acetone, with more difficulty in ether, almost insoluble in petroleum ether and in water.

0.0810 g substance: 0.0030 g  $\text{H}_2\text{O}$  (7 mm., 50-60°).

0.1050 g substance: 0.0042 g  $\text{H}_2\text{O}$  (7 mm., 50-60°).

Found %:  $\text{H}_2\text{O}$  3.70, 4.00.

$\text{C}_{24}\text{H}_{39}\text{O}_7\text{N}\cdot\text{H}_2\text{O}$ : Calculated %:  $\text{H}_2\text{O}$  3.82.

0.0602 g substance in 12 ml chloroform;  $\frac{1}{2}$  = 10.0.

$\alpha_D +0.17^\circ$ ,  $[\alpha]_D^{22} +33.9^\circ$ .

0.1004 g substance: 0.2326 g  $\text{CO}_2$ ; 0.0736 g  $\text{H}_2\text{O}$ .

0.1034 g substance: 0.2426 g  $\text{CO}_2$ ; 0.0804 g  $\text{H}_2\text{O}$ .



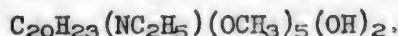
0.0780 g substance: 220 ml N<sub>2</sub> (20°, 726 mm).  
0.1212 g substance: 350 ml N<sub>2</sub> (20°, 726 mm).  
Found %: C 63.18, 63.98; H 8.20, 8.70; N 3.06, 3.14  
C<sub>24</sub>H<sub>39</sub>O<sub>7</sub>N<sub>1</sub>: Calculated %: C 63.54; H 8.67; N 3.09.

#### SUMMARY

1. A mixture of alkaloids was separated from Delphinium biternatum (family Ranunculaceae): from the roots 0.69% and from the above-ground portion 0.62% of the dried weight of the plant.

2. Upon further separating the total alkaloids, two new crystalline bases were obtained: delphatine C<sub>27</sub>H<sub>45</sub>O<sub>7</sub>N and delbine C<sub>24</sub>H<sub>39</sub>O<sub>7</sub>N.

3. On the basis of quantitative determinations of the functional groups, the formula of delphatine may be expanded as:



4. This formula may be contracted to the expression C<sub>20</sub>H<sub>31</sub>, the basic nucleus of several aconite and delphine alkaloids.

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# INVESTIGATION OF THE CATALYTIC CONVERSION OF ALCOHOLS TO HYDROCARBONS OF THE DIVINYL SERIES

## XV. GENERAL MECHANISMS OF THE FORMATION OF DIETHYLENE HYDROCARBONS WITH CONJUGATED SYSTEMIC BONDS

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In our previous papers we presented experimental data relating to the catalytic transformation reactions of ethyl and other alcohols: primary, secondary, tertiary and also binary mixtures of alcohols with carbonyl compounds in contact with the mixed catalyst of S.V. Lebedev [1]. We proposed a scheme for the catalytic formation of divinyl from ethyl alcohol, based on the postulation of an initial dehydrogenation of alcohol to acetaldehyde, followed by the condensation of the aldehyde to crotonaldehyde (probably through aldol) and the further reduction of the crotonaldehyde by the hydrogen of ethyl alcohol to crotylic alcohol, by the dehydration of which divinyl is obtained [2].

- 1)  $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{-CHO} + \text{H}_2$ ,
- 2)  $\text{CH}_3\text{-CHO} + \text{CH}_3\text{-CHO} \rightarrow [\text{CH}_3\text{-CHOH-CH}_2\text{-CHO}] \rightarrow \text{CH}_3\text{-CH=CH-CHO}$ ,
- 3)  $\text{CH}_3\text{-CH=CH-CHO} + 2\text{H} \rightarrow \text{CH}_3\text{-CH=CH-CH}_2\text{OH}$ ,
- 4)  $\text{CH}_3\text{-CH=CH-CH}_2\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2=\text{CH-CH=CH}_2$ .

It was established by a series of experiments that the addition of crotonaldehyde, aldol and acetaldehyde to ethyl alcohol according to the contact method of S.V. Lebedev, results in an increased yield of divinyl [2]. It was also shown that under the influence of the components of S.V. Lebedev's catalyst, acetic acid undergoes condensation with the formation of crotonaldehyde and more complex products [3]

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\* A year after the publication of our paper showing the above scheme and our experimental data, a paper appeared by M. Ya. Kagan, G. D. Lyubarsko and O. M. Podurovsky in the Journal Bulletin of the Academy of Sciences, USSR, Div. of Gen. Chem., No. 2, 173 (1947) entitled Mechanism of the Catalytic Synthesis of Divinyl from Ethyl Alcohol, in which it was stated that our work was conducted to determine the validity of a mechanism proposed by the above authors.

It is needless to say that our investigations showing the possibility of reducing compounds to alcohols under the reaction conditions of S. V. Lebedev, and also work on the explanation of the role of crotonaldehyde as a probable intermediate product in the preparation of divinyl from alcohol, was completed in 1935. The first communication of M. Ya. Kagan, containing a proposed group of possible schemes for the formation of divinyl, including mechanisms which considered crotonaldehyde to be an intermediate product, was published in 1937. By comparing dates it is evident that our investigations preceded the appearance of M. Ya. Kagan's mechanisms, and not the reverse. Thus, the assertions of M. Ya. Kagan, G. D. Lyubarsko and O. M. Podurovsky appears to be a misunderstanding.

Our work was completed before the views of M. Ya. Kagan became known, and the mechanism for the process, described in our previously-published and our present papers, was originated by us on the basis of our previously-obtained experimental data, independently from M. Ya. Kagan.

This statement is confirmed by data and records which are kept in the archives of the All-Union Scientific Research Institute of Synthetic Rubber.

Experiments we conducted together with I.K. Gorn showed that, under the influence of the dehydrated components of S.V. Lebedev's catalyst, crotylic alcohol splits off water at 325 and 375° and is converted to divinyl, the yield of which, under the above conditions, is respectively 54.2 and 51.7 mole % of the alcohol reacted. Thus, we had shown that all the reactions of the above scheme may take place with the components of S.V. Lebedev's catalyst.

Our experiments established that S.V. Lebedev's reaction may be extended also to the higher primary alcohols: propyl and butyl, as well as secondary: isopropyl and secondary butyl [4-8]. The action of the mixed catalyst on the alcohols was, in all cases, analogous to its action on ethyl alcohol. From these alcohols are formed hydrocarbons with conjugated, systemic double bonds, having twice as much carbon atoms in the molecule as the original alcohol.

The formation of divinyl from ethyl alcohol is accompanied by the formation of a group of products among which are acetaldehyde, ethylene and pseudo butylene. The formation of diethylene hydrocarbons from other alcohols is also accompanied by the formation of the primary products of the dehydrogenation and dehydration of the original alcohols, simultaneously obtaining ethylene hydrocarbons having the same number of carbon atoms and the same carbon skeleton as the diethylene hydrocarbon.

Studies of the transformation of isobutyl alcohol showed that the latter, as distinguished from other primary alcohols, propyl and butyl, does not give reaction products with diethylene hydrocarbons and decomposes in two directions: dehydrogenation with formation of isobutyric aldehyde and dehydration with formation of isobutylene [9].

Also investigated were transformations of mixtures of isobutyl alcohol and acetaldehyde [10], ethyl alcohol and acetone [11], ethyl alcohol and methyl ethyl ketone [12], and binary mixtures of methyl alcohol and isopropyl alcohol, methyl alcohol and acetone and mixtures of formaldehyde and isopropyl alcohol [13]. In all these cases the formation of diethylene hydrocarbons, products of mixed condensations, was observed. The number of carbon atoms in the diethylene hydrocarbon molecule obtained was equal to the sum of the carbon atoms in the original alcohol and carbonyl compounds.

Diethylene hydrocarbons are not obtained from tertiary alcohols with the S.V. Lebedev catalyst. The tertiary alcohol splits off water under these conditions, forming the corresponding ethylene hydrocarbon [14].

In the table are given all the results obtained in the investigation of the catalytic transformation of alcohols and binary mixtures of alcohols with carbonyl compounds to hydrocarbons of the divinyl series. In this table are also given fundamental data, which characterized the diethylene hydrocarbons formed (melting point, element composition, molecular weight and several constants for the products of hydrogenation, bromination, hydrobromination and action with maleic anhydride).

The observed differences in yield of the diethylene hydrocarbons for the different alcohols evidently depend on the nature of the alcohol, the composition of the catalyst (ratio of the components) and the conditions for conducting the experiments (temperature, time of contact, etc.). We did not consider it our problem to obtain maximum yields of the diethylene hydrocarbons, but attempted primarily to determine the composition and structure of the basic products of the reaction. A higher yield of the diethylene hydrocarbons may probably be achieved by selecting in individual cases optimum ratios of the components in the mixed catalyst and optimum conditions for the process.

## 865

[illegible]



The data of this table show that the diethylene hydrocarbons obtained from the higher alcohols are formed with a considerably lower yield than divinyl from ethyl alcohol [2]. It may also be noted that the higher the molecular weight of the alcohol, the lower the amount of the diethylene hydrocarbon formed. With equal molecular weights of the original alcohol, the yield of the diethylene hydrocarbon is greater for the primary alcohols than the secondary. It is true that this conclusion is very approximate, since the mixed catalyst used in each case differed somewhat in the ratio of the components and the method of preparation. It should be further noted that the carbon skeleton of the diethylene hydrocarbons formed from primary and secondary propyl alcohols are similar; this may be also noted for the diethylene hydrocarbons obtained from primary and secondary butyl alcohols.

Arising from the supposition that the catalytic formation of diethylene hydrocarbons from alcohols should take place analogously to the conversion of ethyl alcohol to divinyl, in the above-cited works we presented the hypothesis that the processes for the catalytic formation of dienes from alcohols and binary mixtures of different alcohols are realized by means of a conversion to carbonyl compounds followed by condensation to form unsaturated aldehydes (in the case of the primary alcohols), or unsaturated ketones (in the case of the secondary alcohols), with a subsequent reduction to unsaturated alcohols and then dehydration, which results in the formation of conjugated, systemic double bonds.

Analogous schemes were presented for binary mixtures of alcohols and carbonyl compounds. Isobutyl alcohol is incapable of being converted to diethylene hydrocarbons since, although it yields a carbonyl compound (isobutyric aldehyde) upon dehydrogenation, the latter is incapable of condensing into an unsaturated aldehyde [9]. The impossibility of forming an unsaturated aldehyde (condensation product) excludes a further transformation to the diethylene hydrocarbon.

Tertiary alcohols cannot yield diethylene hydrocarbons, since there is no possibility of their forming carbonyl compounds [14].

A possible reason for the decreased yield of diethylene hydrocarbons upon shifting from ethyl alcohol to alcohols with higher molecular weight is the relatively lower mobility of these larger molecules and their decreased capability of desorption from the surface of the catalyst. This situation may result in a longer stay at the surface of the catalyst and thus lead to decomposition or to subsequent condensation.

The structure of the diethylene hydrocarbons have a close genetic relationship to the structure of the original alcohols. Upon collating the experimental material obtained, a group of mechanisms are evident, which conform to the course of the catalytic transformation of alcohols and mixtures of alcohols with carbonyl compounds into diethylene hydrocarbons.

Knowledge of these mechanisms makes it possible to predict the course of reaction for the as yet uninvestigated alcohols and for mixtures of alcohols with the same or other carbonyl compounds thus opening the possibility of obtaining hydrocarbons of any desired structure.

We suppose that the formation of divinyl from a mixture of ethyl alcohol and acetaldehyde on aluminum oxide according to the method of Ostromyslenskii [15] and the catalytic synthesis process for forming divinyl from alcohol according to S.V. Lebedev, take place by the same mechanism, based upon the conception of the condensation of acetaldehyde into crotonaldehyde with its subsequent transformation into divinyl by means of crotylic alcohol. It is probable that the formation of small quantities of divinyl from alcohol in Ipatiev's experiments [16] or the

preparation of divinyl from diethyl ether according to Filippov [17], took place according to the same scheme. In both cases it was accompanied by dehydration and dehydrogenation processes, as a result of which the entire series of transformations shown in our above-presented scheme for the formation of divinyl was realized. From this point of view, the formation of piperylene, observed by Ostromyslenskii, from isopropyl alcohol and acetaldehyde in contact with aluminum oxide [18] may have taken place analogously to the formation of piperylene from a mixture of acetone and ethyl alcohol in contact with the modified catalyst of S.V. Lebedev according to the scheme outlined in one of our previous communications [11]. It is quite possible that heptadiene, discovered by Weizmann and Garrard in the reaction products of a mixture of n-butyl alcohol and acetone in contact with aluminum oxide [19], was also obtained by an identical scheme.

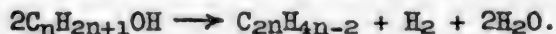
#### GENERAL CONCLUSIONS

1. A mechanism was presented for the catalytic transformation of ethyl alcohol to divinyl, consisting of several successive reactions corresponding to the obtained experimental data:

- 1) ethyl alcohol  $\rightarrow$  acetaldehyde;
- 2) acetaldehyde  $\rightarrow$  (aldol)  $\rightarrow$  crotonaldehyde;
- 3) crotonaldehyde  $\rightarrow$  crotylic alcohol;
- 4) crotylic alcohol  $\rightarrow$  divinyl.

2. It was established that the catalysts used for the preparation of divinyl from ethyl alcohol are also capable of transforming other primary as well as secondary alcohols to hydrocarbons with conjugated systemic double bonds, which contain twice as many carbon atoms as the original alcohol.

The reaction may be expressed by the general equation:



3. Primary alcohols of the type  $R-CH_2-CH_2OH$  are converted to hydrocarbons with conjugated, systemic, double bonds by the condensation of two molecules of aldehyde formed by the dehydrogenation of the alcohol.

The condensation is accompanied by a splitting off of water and the formation of derivatives of crotonaldehyde.

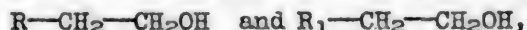
4. The condensation of these aldehydes takes place in such a way that the carbonyl group of one molecule of the aldehyde combines with the carbon atom directly connected with the carbonyl group of the other molecule. Thus from alcohols higher than that of ethyl, diethylene hydrocarbons with a branched chain of hydrocarbon atoms should inevitably be formed.

5. Secondary alcohols of the type  $R-CHOH-CH_3$  are converted to hydrocarbons with conjugated, systemic, double bonds by the condensation of ketones, formed by the dehydrogenation of secondary alcohols, similar to the condensation of acetone into mesityl oxide.

6. In these condensations the ketones react in such a way that the carbonyl group of one molecule of the ketone combines with the methyl group directly connected with the carbonyl group of the other molecule. Thus from secondary alcohols of the above type, 'dienes' with a branched carbon skeleton should inevitably be formed.

7. The formation of diethylene hydrocarbons with conjugated, systemic, double

bonds from mixtures of two different primary alcohols takes place by means of a mixed condensation of the aldehydes obtained by the dehydrogenation of the original alcohols to derivatives of crotonaldehyde. The course of the condensation reaction in the general case of a binary mixture of alcohols:



cannot yet be considered definitely established because of insufficient experimental data.\* However, for a mixture of two primary alcohols, one of which is ethyl, it may be considered that in the condensation reaction there participate the methyl group of acetaldehyde formed from ethyl alcohol, and the carbonyl group of the aldehyde formed from the other alcohol.

Where the second alcohol has a normal hydrocarbon skeleton, a 'diene' with a straight chain should be formed. The amount of carbon atoms in the 'diene' formed is equal to the sum of the carbon atoms contained in both molecules of the alcohols taken.

8. From mixtures of alcohols with differentyl situated hydroxyl groups (primary and secondary), under suitable conditions there should also be obtained diethylene hydrocarbons with conjugated bonds.

The reaction also evidently takes place by means of a mixed condensation of an aldehyde and a ketone obtained by the dehydrogenation of the alcohols taken, and is accompanied by a splitting off of water. In the formation of diethylene hydrocarbons from a mixture of primary alcohol and ketones of the type  $CH_3-CO-R$  (or, similarly, from a mixture of a primary alcohol and a secondary of the type  $CH_3-CHOH-R$ ) the condensation takes place in such a way that the carbonyl group of the aldehyde formed from the primary alcohol, being more active, condenses with the methyl group directly connected with the carbonyl group of the ketone.

In this case the diethylene hydrocarbon formed should possess a straight chain of carbon atoms if the original substance had a normal skeleton.

9. The intermediate unsaturated aldehyde (for primary alcohols) or unsaturated ketone (for secondary alcohols or for a mixture of a secondary alcohol and a primary) formed by condensation and cleavage of water undergoes reduction by the hydrogen given off from the original alcohol, being converted to its corresponding unsaturated alcohol by a reduction similar to that of crotonaldehyde to crotylic alcohol.

10. In the dehydration of the intermediate, unsaturated alcohol, an intramolecular regrouping takes place with the formation of a conjugated system of double bonds. The position of the conjugated system in the molecule depends upon the positions of the ethylene bond and the hydroxyl group in the unsaturated alcohol.

In individual cases it is possible to form a mixture of isomeric diethylene hydrocarbons with conjugated bonds and to shift the conjugated system from the terminal atoms to the central portion of the hydrocarbon molecule.

11. Primary alcohols yielding carbonyl compounds but incapable of forming unsaturated aldehydes by condensation (derivatives of crotonaldehyde, for example isobutyl alcohol), do not form diethylene hydrocarbons with conjugated bonds.

12. Tertiary alcohols do not form diethylene hydrocarbons with conjugated bonds, since they are incapable of being converted to carbonyl compounds with their subsequent condensations. The only possible course of reaction is the dehydration of the tertiary alcohol with the formation of the corresponding ethylene hydrocarbon.

\* Probably a mixture of isomeric diethylene hydrocarbons with conjugated bonds may be formed in this case.

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\* Consultants Bureau English Translation, page 625.



# ACTION OF ALCOHOLS ON THE $\alpha$ -OXIDES OF BICYCLIC TERPENES

## I. Action of Alcohols on $\alpha$ -Pinene Oxide

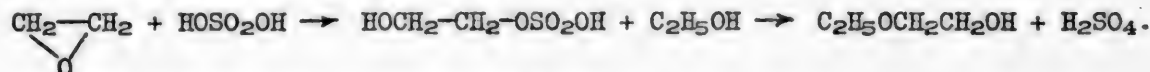
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Laboratory of Organic Chemistry of the A.M. Butlerov Scientific Research  
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The action of alcohols on the simplest olefin oxides - ethylene and propylene oxides - has been studied in detail due to the fact that this reaction is the basis for the commercial production of monoalkyl ethers of glycols - cellosolves. The reaction is catalyzed by acids [1]. The sulfates of polyvalent elements such as nickel, zinc, chromium [2], dialkylsulfates [3], hydrosilicates [4], boron fluoride [5], and substances of an alkaline nature [6] have all been proposed as catalysts.

These works are principally patents. The question of the mechanism of the reactions between alcohols and  $\alpha$ -oxides have until recently been very inadequately explained.

Fourneau and Ribas [7] present a mechanism for the catalytic action of sulfuric acid using the formation of esters of sulphuric acid as intermediate products according to the equation:



This scheme was adopted by Smith and Niederl [8].

Still less attention has been turned to the series of combinations of alcohols with unsymmetrically substituted oxides.

It was believed that in this case ethers of primary-secondary groups are obtained (Davidson [9], Dewael [10], etc.).

However, Cox, Nelson and Cretcher [11] in 1927 showed that on heating propylene oxide with n-propyl alcohol in the presence of a catalyst a heterogeneous propyl ether of propyleneglycol is obtained.

In 1934 Edlund [12] showed that tertiary ethers of isobutylene-glycol are obtained by the action of alcohols on isobutylene oxide in the presence of sulfuric acid. Sparks and Nelson [13] showed that this reaction in the absence of catalysts results in a mixture of two possible isomeric ethers.

The influence of catalysts on the series of compounds formed with alcohols and unsymmetrical oxides was first discovered by A.A. Petrov and A.A. Tyazhelova [14] using isobutylene oxide as an example. On heating isobutylene oxide with alcohols in the presence of alcoholates A.A. Tyazhelova [14] obtained primary ethers of isobutyleneglycol. By the action of boron fluoride on alcoholic solutions of isobutylene oxide, A.A. Petrov [15] obtained tertiary ethers. A.A. Petrov explains the catalytic action of boron fluoride by the formation of a complex with the oxides.

In a subsequent work A.A.Petrov [15] obtained additional data on the influence of catalysts on the series of compounds of alcohols and propylene oxide. He showed that by the action of alcoholates, propylene oxide and alcohols form primary ethers of propylene glycol. The ethers obtained by the action of sulfuric acid or boron fluoride as catalysts, or by heating oxides with alcohols under pressure, are mixtures of primary and secondary ethers.

According to A.A.Petrov, in the undistorted molecules of propylene oxide and isobutylene, the bond between oxygen and the tertiary carbon atom is easily broken under the influence of the + I effect of the methyl groups, with the formation of secondary or the corresponding tertiary hydroxyl groups.

Concerning the catalytic action of acids or boron fluoride, the oxygen bond is weakened under the influence of the proton coordination due to the unused oxygen electrons. By such a coordination these catalysts induce a positive charge on the oxygen atom, as a result of which the stability of the bond between the oxygen and the tertiary carbon atom is increased. Chitwood and Freure [18] have presented a similar mechanism on the influence of catalysts on the series of compounds formed by the addition of alcohols to oxides.

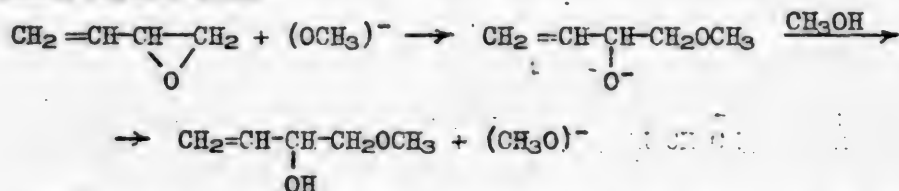
According to the experiments of Chitwood and Freure propylene oxide, in the presence of the ethylate of sodium or tributylamine, forms with alcohols primary ethers exclusively; in the presence of sulfuric acid, boron fluoride or by heating without catalysts a mixture of both isomers is formed.

Thus, similarly to A.A.Petrov, Chitwood and Freure suppose that in the acid-catalyzed reaction a proton attaches itself to the oxygen bridge, weakening the C-O bond at which the alcohol molecule becomes attached. In the base-catalyzed reaction the alkoxyl ion exerts a nucleophilic influence principally on the primary carbon atom which possesses a lower electronic density. 1-alkoxylpropanol-2- is obtained.

In 1946 Kadash [17] studied in detail the reaction of divinyl oxide with methyl alcohol under different conditions in order to explain the influence of various factors on the cleavage of the oxide ring.

According to Kadesh's observations the reaction of oxides with alcohols may be of a bimolecular or monomolecular type. Kadesh calls the first type a normal reaction, the second an abnormal one.

The addition of alcohols in the presence of basic catalysts usually conforms with the normal type of reaction. The nucleophilic reagent acts on the least substituted carbon atom.



In the presence of acids the reaction proceeds bimolecularly as well as monomolecularly with the formation of normal and abnormal products.

The monomolecular ring cleavage proceeds according to the scheme:



After separation of the hydroxyl-containing components by treatment with sodium a compound of the composition  $C_{12}H_{22}O_2$  was separated from the products of the reaction,

m.p. 100-102° (14 mm);  $n_D^{20}$  1.4624;  $d_4^{20}$  0.9414;  
found: MR 57.86;  $C_{12}H_{22}O_2$  F. Calculated: MR 58.23.

The compound does not contain hydroxyl groups and according to the molecular refractivity and data from titration with perphthalic acid, it contains a double bond.

It was previously shown (B.A. Arbuzov [19]) that  $\alpha$ -pinene oxide undergoes isomeric conversion to campholene aldehyde under the catalytic influence of zinc chloride and bromide.

On the basis of these works it was natural to postulate that in the presence of sulfuric acid an isomerization of  $\alpha$ -pinene oxide to campholene aldehyde takes place, which in the presence of alcohol and sulfuric acid gives acetal. A study of the chemical properties of the product we separated, b.p. 100-102° (14 mm) confirmed this postulation.

On hydrolyzing it with 8% hydrochloric acid campholene aldehyde was obtained which gave a semicarbazone with a m.p. 138-139°, identical with the semicarbazone of campholene aldehyde.

From the higher-boiling fractions of the products of the reactions of methyl alcohol with  $\alpha$ -pinene oxide a fraction was separated with a b.p. of 126-131° (11.5 mm);  $n_D^{20}$  1.4859;  $d_4^{20}$  1.000. Analysis of this product closely corresponds to the formula  $C_{11}H_{20}O_2$ . According to the molecular refraction and titration with perphthalic acid the substance contains one double bond. A determination of the hydroxyl group, according to the method of Chugaev - Tserevetinov, showed the presence of one hydroxyl group. All these data indicate that the fraction 126-131° (11.5 mm) consists of a monomethyl ether of an unsaturated glycol.

Analogous results were obtained by the action of ethyl and propyl alcohols on  $\alpha$ -pinene oxide in the presence of sulfuric acid.

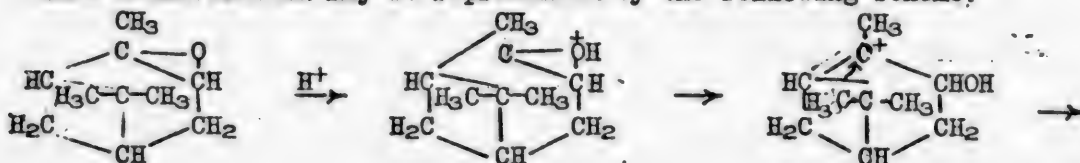
In the case of the reaction of  $\alpha$ -pinene oxide with ethyl alcohol, the ethyl acetal of campholene aldehyde was obtained as the principal product of the reaction:

b.p. 88-89° (5.5 mm);  $n_D^{20}$  1.4646;  $d_4^{20}$  0.9234; found: MR 67.61;  
 $C_{14}H_{26}O_2$  F. Calculated: MR 67.47.

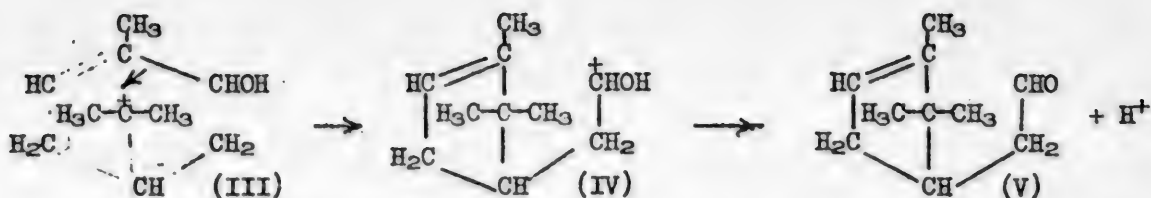
on hydrolysis giving campholene aldehyde (semicarbazone m.p. 137°) and higher-boiling fractions which were not investigated more closely because of the small quantity obtained.

Obtaining the acetal of campholene aldehyde and the monoether of an unsaturated glycol by the action of methyl alcohol on pinene oxide, as well as substances we obtained from other bicyclic terpene oxides lead us to the following scheme explaining the course of reaction between  $\alpha$ -pinene oxide and alcohols in the presence of sulfuric acid. By the action of sulfuric acid  $\alpha$ -pinene oxide isomerizes to campholene oxide.

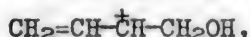
This isomerization may be represented by the following scheme:



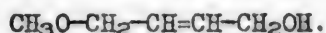




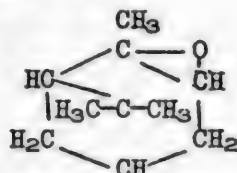
Such a monomolecular cleavage of the oxide ring under the influence of the 'onium complex' (I) formed by the addition of a hydrogen ion agrees with all the data found in a survey of the literature. The possibility of a monomolecular oxide ring cleavage becomes more probable if a carbonium ion is formed or additional stability is obtained because of resonance. Thus, in the case of divinyl oxide in the presence of acids, for the carbonium ion formed:



another structure  $\overset{+}{\text{C}}\text{H}_2-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$  is possible. Indeed, by the action of methyl alcohol Kadesh obtained a small quantity of a product corresponding in its properties to 4-methoxy-2-butenol-1:



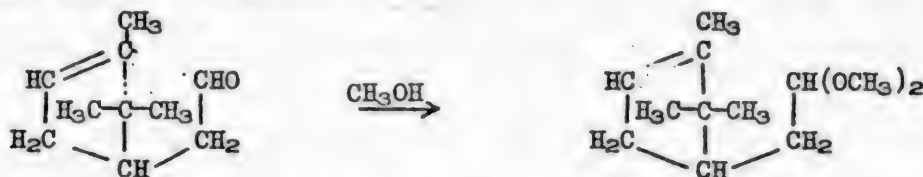
In the case of  $\alpha$ -pinene oxide the role of the double bond, connected with the oxide ring of divinyl oxide is played by the unstable cyclobutane ring of  $\alpha$ -pinene connected to the oxide ring,



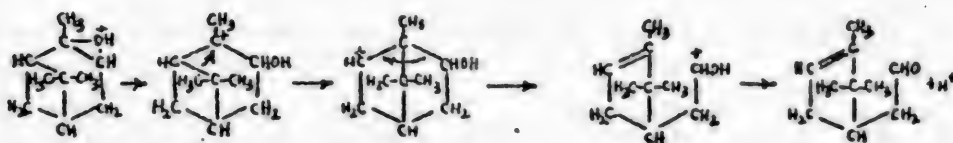
which leads in this case to the formation of a structure with a positive charge at the 6-carbon (III).

The shift to (II) and (III) is promoted by the  $\pm$ I effect of the two methyl groups at the 6-carbon.

In the presence of sulfuric acid campholene aldehyde [or ion (IV)] gives the acetal with methyl alcohol:

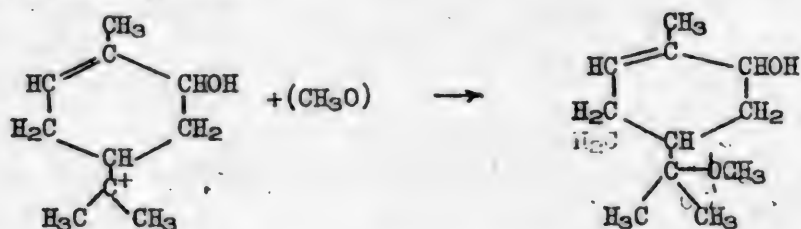


\* Besides the scheme indicated for the isomerization of  $\alpha$ -pinene oxide to campholene aldehyde the following course is also possible.



As was shown above, from the higher-boiling fractions of the reaction products of  $\alpha$ -pinene with methyl alcohol a product was separated closely corresponding in its analysis to an unsaturated monomethyl ether of glycol.

The most probable structure of this compound is that of a monomethyl ether of sobrerol, which could be formed from the carbonium ion (III) by the addition of a methoxyl ion:



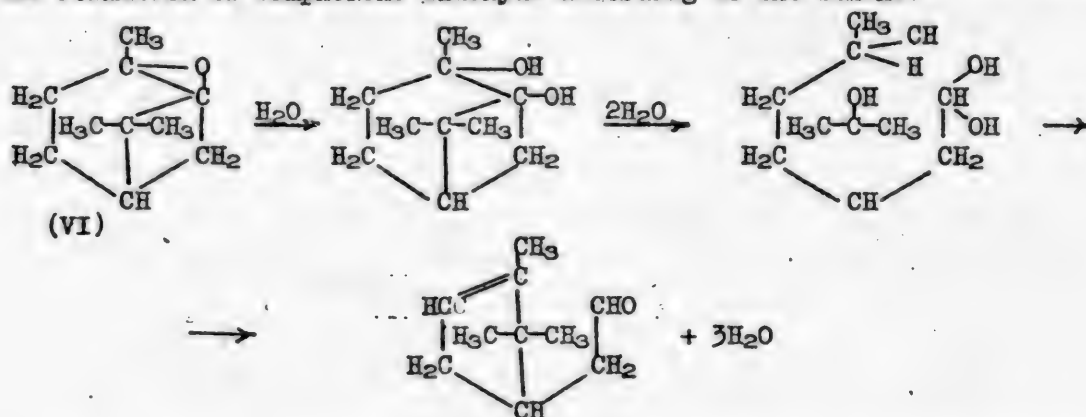
We were not able to obtain the monomethyl ether of glycol in an analytically pure state since it was contaminated with a small amount of an impurity, evidently sobrerol, produced by the addition of a hydroxyl ion to (III) due to the water separated by the formation of the acetal.

The question of the nature of the product with a b.p. of  $126-131^\circ$  (11.5 mm) requires further development, although its indicated structure as a tertiary ether of sobrerol is quite probable.\*

The proposed scheme permits a simple representation of the hydration of  $\alpha$ -pinene oxide to form sobrerol, first observed by N.A. Prilezhaev [20], and the further formation of small quantities of campholene aldehyde [21].

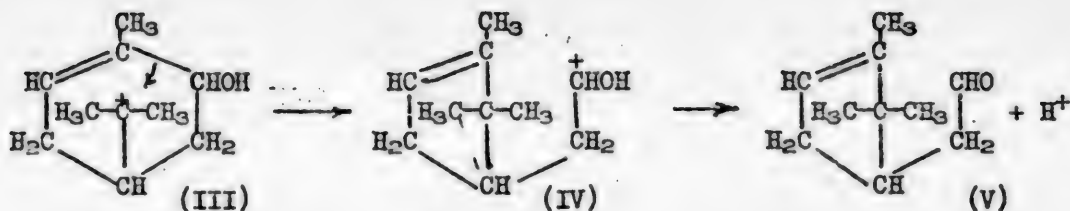
Sobrerol is formed by the addition of a hydroxyl ion to the carbonium ion (III). To explain the formation of campholene aldehyde by the hydration of  $\alpha$ -pinene oxide in an acid medium Prilezhaev and Vershuk [21] assume the presence of a hypothetical isopinene oxide (VI) in  $\alpha$ -pinene oxide.

According to Prilezhaev and Vershuk, the hydration of isopinene oxide leads to the formation of campholene aldehyde according to the scheme:



As is evident from the above statements, campholene aldehyde may be formed in small quantities by the hydration of  $\alpha$ -pinene oxide because of the conversion of (III) to (V), there being no necessity of assuming the existence of a hypothetical isopinene.

\* An explanation of the possibility of forming normal derivatives of pinene glycol ethers by the action of  $\alpha$ -pinene with alcohols requires a further, more detailed study of the hydroxyl-containing products of the reaction.



#### EXPERIMENTAL

$\alpha$ -Pinene oxide was obtained by the oxidation of  $\alpha$ -pinene with acetyl hydrogen peroxide and had: b.p.  $61-62^\circ$  (10 mm);  $n_D^{20}$  1.4687;  $d_4^{20}$  0.9656;  $[\alpha]_D^{20} + 67.58^\circ$ .

#### Action of Methyl Alcohol on $\alpha$ -Pinene Oxide in the Presence of Sulfuric Acid

58 g of pinene oxide, 50 g of anhydrous methyl alcohol and 0.3 g of concentrated sulfuric acid were taken for the reaction.

Pinene oxide was gradually added to the methyl alcohol, containing the sulfuric acid. The reaction proceeded with liberation of heat and the temperature rose to  $46^\circ$ . After standing for three hours the sulfuric acid was neutralized with sodium methylate, the methyl alcohol was distilled off and the residue subjected to fractional distillation in vacuo.

In the first distillation the following fractions were obtained.

- 1)  $90-105^\circ$  (12.5 mm) 2.3 g.  $n_D^{20}$  1.4650;
- 2)  $105-118^\circ$  (12 mm) 32.5 g.  $n_D^{20}$  1.4693;
- 3)  $118-140^\circ$  (12 mm) 20.5 g.  $n_D^{20}$  1.4852;

Notwithstanding numerous distillations we could not separate the individual products.

From the lower-boiling fractions 21.5 g of a fraction with a b.p.  $98-107^\circ$  (11 mm) could be separated;  $n_D^{20}$  1.4678. By further distillation 13 g was obtained boiling at  $96-101^\circ$  (11 mm),  $n_D^{20}$  1.4638.

By distilling the higher-boiling fractions 17.4 g of a fraction b.p.  $125-132^\circ$  (12 mm) was separated;  $n_D^{20}$  1.4847. Upon further fractionation a  $126-131^\circ$  (11.5 mm) fraction was separated. The  $96-101^\circ$  (11 mm) fraction had the following constants:

$$n_D^{20} 1.4638; d_4^{20} 0.9400; \alpha_D^{20} + 20.75^\circ.$$

Determination of the hydroxyl group, according to the method of Chugaev-Tserevitinov, gave:

Found OH %: 5.07, 4.81.

$C_{11}H_{20}O_2$ . Calculated OH %: 9.26.

This fraction was distilled over sodium and had:

B.p.  $100-102^\circ$  (14 mm);  $n_D^{20}$  1.4624;  $d_4^{20}$  0.9414; MR 57.86.

$C_{12}H_{22}O_2$ . Calculated: MR 58.23.

0.0808 g substance: 0.2146 g  $CO_2$ ; 0.0820 g  $H_2O$ .

Found %: C 72.43; H 11.27.

$C_{12}H_{22}O_2$ . Calculated %: C 72.66; H 11.18.

Analysis of the fraction for unsaturation by titration with perchthalic acid:

0.0956 g, 0.0878 g substance.  
Calculated active oxygen for  $C_{12}H_{22}O_2 F_1$ .  
0.00772 g, 0.00709 g:  
Found 0.00767 g, 0.00701 g.

Hydrolysis of the 100-102° (14 mm) Fraction. 3 g of the fraction was heated with 8% hydrochloric acid (10 ml) for 30 minutes on a heated water bath at 60-68° and then distilled in vacuo. The oily layer formed was separated from water and treated with semicarbazide. From 1 g of the hydrolysis product, 1 g of sodium acetate, and 0.9 g of semicarbazide hydrochloride, was obtained 1 g of impure semicarbazone. After two recrystallizations from ethyl acetate, b.p. 137-138°. Upon admixture of the sample with the semicarbazone of campholene aldehyde, the melting point was not changed. The intermediate fractions boiling over 102° at 12 mm within the limits 103-113° (11 mm) were treated with boric acid to remove hydroxyl-containing compounds. After the treatment the dimethyl acetal of campholene aldehyde was separated with

b.p. 101-104° (14 mm);  $n_D^{20}$  1.4590;  $d_4^{20}$  0.9302,  
giving campholene aldehyde upon hydrolysis (semicarbazone m.p. 137-138°).

Investigation of the 126-131° (11.5 mm) Fraction. The fraction 126-131° (11.5 mm) had the following constants:

$n_D^{20}$  1.4859;  $d_4^{20}$  1.0000; MR found 52.82;  $C_{11}H_{20}O_2 F_1$ . calculated MR 53.49.

0.1902 g substance: 0.4946 g  $CO_2$ ; 0.1864 g  $H_2O$ .

Found %: C 70.92, H 10.88.

$C_{11}H_{20}O_2$ . Calculated %: C 71.74, H 10.87.

Determination of the hydroxyl group, according to Chugaev-Tserevitinov, gave the following results:

Found %: OH 10.61, 10.33.

$C_{11}H_{20}O_2$ . Calculated %: OH 9.26.

Determination of unsaturation by titration with perphthalic acid gave the active oxygen:

0.0978 g, 0.0616 g substance: found 0.00681 g, 0.00542 g, or 1.02 double bonds:  $C_{11}H_{20}O_2 F_1$ . Calculated active oxygen 0.00663 g; 0.00531 g.

The experiment on the action of methyl alcohol on  $\alpha$ -pinene oxide in the presence of sulfuric acid was repeated. 50 g of  $\alpha$ -pinene oxide, 52.6 g of methyl alcohol and 0.3 g of sulfuric acid were taken for the reaction. The 95-140° (9 mm) fraction obtained after neutralizing the sulfuric acid, distilling off the alcohol and distilling the residue in vacuo was treated with boric acid. 48 g of the 95-140° (9 mm) fraction and 3.4 g of boric acid were heated for 3 hours under vacuum. The portion of the 95-140° (9 mm) fraction which did not react with boric acid gave 21.6 g of a substance upon distillation, b.p. 101-103° (11.5 mm), which is 45% of the total weight of the mixture of the reaction products.

#### Action of Ethyl Alcohol on $\alpha$ -Pinene Oxide in the Presence of Sulfuric Acid

12 g of  $\alpha$ -pinene oxide, 13 g of absolute alcohol containing 0.3 g of sulfuric acid were taken. Upon addition of the oxide the temperature rose from 17 to 40°. After neutralizing the sulfuric acid with sodium ethylate, distilling off the alcohol and distilling in vacuo, 9.4 g of a fraction was obtained with b.p. = 90-114° (5 mm). A second fractionation gave 6 g of a 85-87° (6 mm) fraction and 3 g of a 97-114° (5 mm) fraction. Upon redistilling the first fraction over sodium 4.1 g of a fraction was obtained with



b.p. 88-89° (5.5 mm);  $n_D^{20}$  1.4646;  $d_4^{20}$  0.9234; MR found 67.61.

$C_{14}H_{26}O_2$  F<sub>1</sub>. Calculated: MR 67.47.

0.0956 g substance: 0.2952 g CO<sub>2</sub>; 0.0984 g H<sub>2</sub>O.

Found %: C 73.94; H 11.43.

$C_{14}H_{26}O_2$ . Calculated %: C 74.34; H 11.50.

Analysis for unsaturation by titration with perphthalic acid: 0.1644 g substance. active oxygen found 0.01150 g, or 0.98 double bond.

$C_{14}H_{26}O_2$ . Calculated active oxygen 0.01163 g, 0.1480 g substance: active oxygen found 0.01007 g, or 0.96 double bond.

$C_{14}H_{26}O_2$ . Calculated active oxygen 0.01047 g.

On hydrolysis with 8% hydrochloric acid campholene aldehyde was obtained (semicarbazone m.p. 138-139°).

#### SUMMARY

1. The action of methyl and ethyl alcohols on  $\alpha$ -pinene oxide in the presence of sulfuric acid was studied.

2. It was shown that the alcohol addition reaction is accompanied by an isomerization of the oxide. The principal reaction products are the corresponding methyl and ethyl acetals of campholene aldehyde. In the case of methyl alcohol, a methyl ether of an unsaturated glycol was separated from the higher-boiling fractions, the structure of which is believed to be that of tertiary methyl ether or sobrerol.

3. An interpretation was given for the isomerization processes of  $\alpha$ -pinene oxide under the influence of acids and the addition of alcohol from the point of view of the formation of 'oxonium complexes' of pinene oxide with hydrogen ion.

From this point of view, interpretations were presented for the hydration of  $\alpha$ -pinene oxide to sobrerol and for the simultaneous formation of campholene aldehyde.

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# ACTION OF ALCOHOLS ON THE $\alpha$ -OXIDES OF BICYCLIC TERPENES

## II. ACTION OF ALCOHOLS ON $\Delta^3$ -CARENE AND CAMPHENE OXIDES

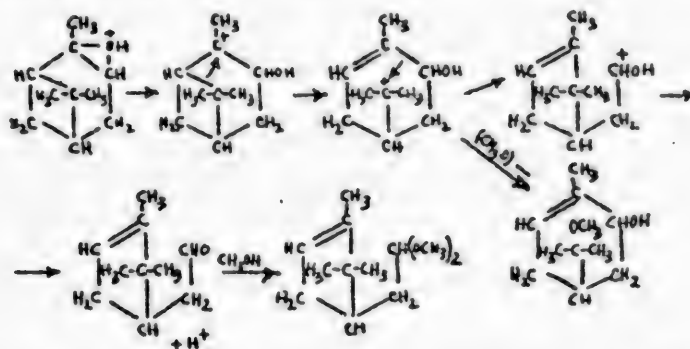
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In a previous paper [1] data were presented on the action of alcohols on  $\alpha$ -pinene oxide in the presence of sulfuric acid. The reaction is accompanied by an isomerization of pinene oxide to campholene aldehyde, which gives the corresponding acetal with an alcohol. In the case of methyl alcohol there was separated, together with the acetal, a monomethyl ether of an unsaturated glycol, to which we assigned the structure of a tertiary methyl ether of sobrerol.

The transformations taking place by the action of an alcohol on  $\alpha$ -pinene oxide in the presence of sulfuric acid are easily explained from the point of view of a monomolecular cleavage of the onium complex, obtained by the combination of a hydrogen ion to the oxide oxygen.

The formation of derivatives of campholene aldehyde and sobrerol is explained, according to the reaction scheme presented, by the coupling of the unstable cyclobutane ring to the oxide ring:

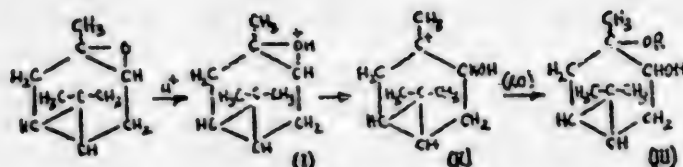


From the point of view of the statements presented in communication I on the mechanism of the transformations taking place by the action of alcohols on bicyclic terpene oxides in the presence of sulfuric acid, the oxide of  $\Delta^3$ -carene is of especial interest.

$\Delta^3$ -Carene oxide contains a bicyclic system with an unstable cyclopropane ring, not connected to the oxide ring. In this case it was expected that by the action with alcohols in the presence of acidic catalysts the complex transformations which take place in the case of  $\alpha$ -pinene oxide would not occur, and the chief product of the reaction should be the monoether of carene glycol.

A. A. Petrov's data, given in communication I, on the addition of alcohols to isobutylene oxide in the presence of acid catalysts permit one to expect the formation of a tertiary ether of carene glycol in the case of  $\Delta$ -carene oxide,

according to the scheme:



In the present paper are presented data we obtained on the action of various alcohols on  $\Delta^3$ -carene oxide, which are in complete agreement with our earlier developed views on the mechanism of the action of alcohols on the  $\alpha$ -oxide.

By the action of methyl alcohol on  $\Delta^3$ -carene oxide in the presence of sulfuric acid a product was obtained with the composition  $C_{11}H_{20}O_2$ :

b.p.  $112^\circ$  (11.5 mm);  $d_4^{20}$  1.0065;  $n_D^{20}$  1.4794; MR 51.89.

$C_{11}H_{20}O_2$  with a three-membered ring calculated MR 52.24.

As is shown by the molecular refraction, the reaction product does not contain a double bond, which was also confirmed by oxidizing the compound with perphthalic acid. Analysis, according to Chugaev-Tserevitinov, indicated the presence of one hydroxyl group. The ability of the product obtained to esterify with boric acid indicates the secondary and not the tertiary nature of the hydroxyl group.

All these data show that the compound obtained is tertiary monomethyl ether of carene glycol (III, R =  $CH_3$ ).

By the action of ethyl, n-propyl and n-butyl alcohols on carene oxide tertiary ethers of carene glycol were obtained. Their constants are given in the table:

Ether	Boiling point	$n_D^{20}$	$d_4^{20}$	MR calculated	MR found
Methyl . . . . .	$112^\circ$ (11.5 mm)	1.4794	1.0065	52.24	51.89
Ethyl . . . . .	$93.5-94^\circ$ (4.5 mm)	1.4758	0.9852	56.86	56.60
n-Propyl . . . . .	$96-98^\circ$ (4 mm)	1.4728	0.9692	61.48	61.33
Iso-propyl . . . . .	$104-106^\circ$ (6.5 mm)	1.4737	0.9715	61.48	61.30
n-Butyl . . . . .	$111-113^\circ$ (4.5 mm)	1.4726	0.9628	66.10	65.78

The reaction of  $\Delta^3$ -carene oxide with secondary alcohols in the presence of sulfuric acid is accompanied by a partial isomerization of  $\Delta^3$ -carene oxide to form an unsaturated aldehyde, the semicarbazone of which has a m.p. of  $216-217^\circ$ . Thus, by the action of isopropyl alcohol on  $\Delta^3$ -carene oxide a product was obtained of the composition  $C_{10}H_{16}O$  with the following constants:

B.p.  $74-76^\circ$  (5 mm);  $d_4^{20}$  0.9320;  $n_D^{20}$  1.4711; MR 45.59.

$C_{10}H_{16}OF_1$ . Calculated MR: 45.76.

These constants closely agree with the constants of the unsaturated aldehyde previously obtained (B.A. Arbuzov [2]) by the isomerization of  $\Delta^3$ -carene oxide in the presence of zinc bromide:

B.p.  $59-59.5^\circ$  (3 mm);  $n_D^{17}$  1.4708;  $d_4^{17}$  0.9311; MR 45.61.

From the higher-boiling fractions a product was separated, corresponding in all its properties to a tertiary isopropyl ether of carene glycol. Its constants



are given in the table.

Thus, with secondary alcohols in the presence of sulfuric acid  $\Delta^3$ -carene oxide reacts in two directions: with the formation of a normal reaction product for the addition of the alcohol to the oxide and with the formation of an unsaturated aldehyde, resulting from an isomerization of the oxide, identical to that obtained by the isomerization of  $\Delta^3$ -carene oxide under the influence of zinc bromide.

The structure of the unsaturated aldehyde has to date not been established. The only course of reaction for  $\Delta^3$ -carene oxide with tertiary butyl alcohol in the presence of sulfuric acid is the isomerization of the oxide to form the unsaturated aldehyde. In this case the reaction does not proceed as energetically and requires heating to 65-70°. A fraction was separated from the reaction products with a b.p. of 63-73° (5 mm),  $n_D^{20}$  1.4725;  $d_4^{20}$  0.9340, similar in constants to the aldehyde separated by the action of isopropyl alcohol on carene oxide. The fraction contains one double bond. By the action of semicarbazide a semicarbazone was obtained with a m.p. of 221-222°, not depressing the melting point when admixed with the semicarbazone, m.p. 216-217°, obtained in the experiment with isopropyl alcohol.

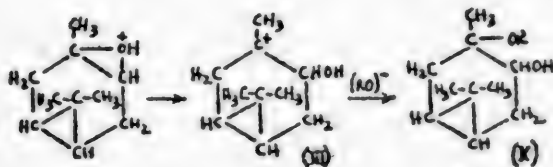
Thus, the following generalities are observed for the action of  $\Delta^3$ -carene oxide with alcohols in the presence of sulfuric acid: primary alcohols react with the formation of normal products of the addition of alcohols to the oxide; by the action of secondary alcohols a partial isomerization of the oxide takes place to form an aldehyde; by the action of tertiary alcohols the isomerization of the oxide becomes the principal course of reaction.

By such a generality it may be possible to explain the different concentrations of the corresponding alkoxyl ions in the reaction mixture.

As was found by McEwen [3], alcohols are arranged in the following order, according to the degree of dissociation to alkoxyl anions and protons:

primary > secondary > tertiary.

The large concentration of alkoxyl anions results from the normal course of reaction of primary alcohols with  $\Delta^3$ -carene oxide in the presence of sulfuric acid:



In the case of secondary alcohols, due to the fact that the concentration of alkoxyl ions is insufficient for a complete conversion of the carbonium ion (III) to the ether (IV), a partial isomerization of the ion to the unsaturated aldehyde becomes possible.

The negligible concentration of alkoxyl ions in the case of tertiary alcohols makes the isomerization of  $\Delta^3$ -carene oxide the principal course of the reaction.

In order to verify the possibilities of isomerization of  $\Delta^3$ -carene oxide under the influence of sulfuric acid an experiment was conducted on the action of small quantities of sulfuric acid in a medium of dry benzene. Since sulfuric acid is difficultly soluble in benzene the reaction did not take place smoothly. A

fraction was obtained with constants corresponding to the above-mentioned unsaturated aldehyde:

B.p. 62-67° (5 mm);  $d_4^{20}$  0.9331;  $n_D^{20}$  1.4726; MR 45.62.

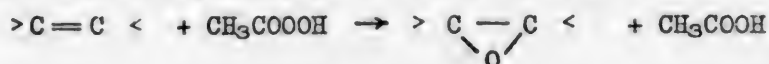
$C_{10}H_{16}O_1F_1$ . Calculated MR: 45.76.

The semicarbazone obtained from the 62-67° (5 mm) fraction had a m.p. of 216-217°.

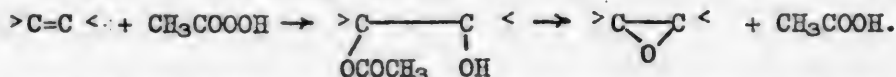
An explanation of the structure of the products obtained by the action of terpene oxides with alcohols affords the possibility of still another method for determining the course of oxidation of unsaturated compounds of hydroperoxy acids.

Two views exist on the oxidation of unsaturated compounds by acetyl hydroperoxide and other hydroperoxy acids.

I. The oxides are the primary products of oxidation:



II. First the molecule of acetyl hydroperoxide adds on at the double bond. The oxides appear as secondary products:



In the case of the formation of oxides as primary products of the reaction with hydroperoxide, if the oxidation reaction is carried out in an alcoholic medium, the formation of the same products as those formed by the action of alcohols on the corresponding oxide may be expected. If the primary product is a glycol monoacetate, it would hardly yield the same products by the action of alcohols as would the oxide.

In the oxidation of  $\Delta^3$ -carene by acetyl hydroperoxide in a medium of absolute alcohol in the presence of sulfuric acid the monoethyl ether of carene glycol was obtained as the principal reaction product, with the following constants:

b.p. 103-104° (6 mm);  $d_4^{20}$  0.9855;  $n_D^{20}$  1.4753; MR 56.58.

$C_{12}H_{22}O_2$ . Calculated MR: 56.86.

identical with the constants of the ethyl ether obtained from carene oxide.

Besides a tertiary monoethyl ether of carene glycol, a small quantity of a crystalline product was separated with a m.p. of 73-75°, which proved to be carene glycol. The formation of carene glycol is explained by the hydration of the oxide by traces of water under the influence of sulfuric acid.

Thus, the data obtained confirm our earlier-stated opinion (B.A.Arbutov[4]) that the oxides are primary products of the reaction of unsaturated compounds with acid hydroperoxides.

#### Action of Methyl Alcohol on Camphene Oxide in the Presence of Sulfuric Acid

As was found by Faidutti[5], camphene oxide isomerizes to camphenilane aldehyde upon distillation over pumice or silica. It was shown by B.A.Arbutov that by distilling camphene oxide over zinc bromide, it isomerizes smoothly to form camphenilane aldehyde. Therefore, in studying the reaction between camphene oxide and alcohols in the presence of sulfuric acid it was expected that derivatives of camphenilane aldehyde would be formed together with the normal products of the addition of alcohols at the oxide ring.

Experiments we conducted on the action of methyl alcohol on camphene oxide

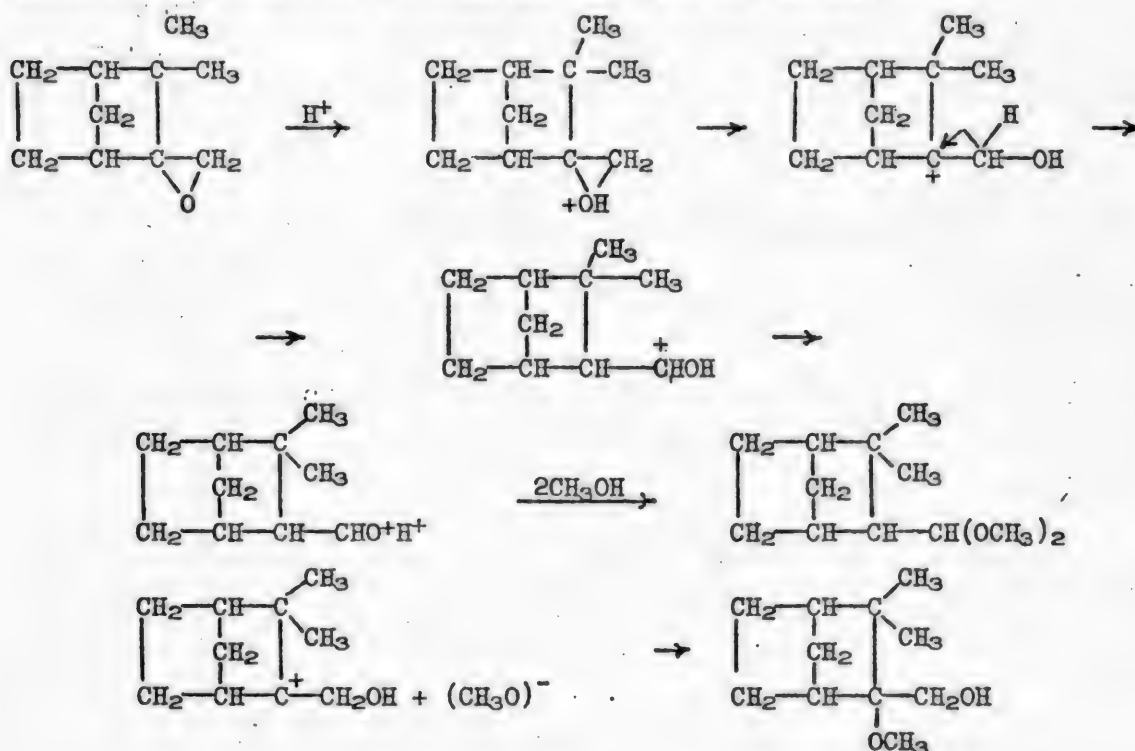
in the presence of sulfuric acid showed that the principal product of the reaction is a saturated compound of the composition  $C_{12}H_{22}O_2$  with the following constants:

B.p. 103-105° (16 mm);  $n_D^{20}$  1.4654;  $d_4^{20}$  0.9760;  $[\alpha]_D^{20}$  -726°; MR 56.07.  
C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>. Calculated: MR 56.50.

On hydrolysis with 8% hydrochloric acid the compound obtained was camphenilane aldehyde with a m.p. of 63-65°, which gave a semicarbazone with a m.p. 190-191°.

Thus, the principal product of the reaction proved to be the dimethyl acetal of camphenilane aldehyde. Besides the acetal a small quantity of a substance with a m.p.  $84^{\circ}$  was separated from the reaction products, corresponding to the composition ( $C_{11}H_{20}O_2$ ) and containing a hydroxyl group. As shown by the experiment the product with a m.p. of  $84^{\circ}$  esterifies with boric acid and thus contains a primary alcohol group.

The reaction between camphene oxide and methyl alcohol in the presence of sulfuric acid therefore proceeds according to the scheme:



## EXPERIMENTAL

The carene oxide was prepared by oxidizing  $\Delta^3$ -carene with acetyl hydroperoxide.  $\Delta^3$ -Carene was separated from turpentine sulfate by fractionation in a column 1.5 m high, with an efficiency of 30 theoretical plates, and had:

b.p. 167-168° (749 mm);  $n_D^{20}$  1.4720;  $d_4^{20}$  0.8647;  $\alpha_D^{20}$  +13.12°;  
 $\Delta^3$ -carene oxide; b.p. 54-56° (5 mm);  $n_D^{20}$  1.4653;  $d_4^{20}$  0.9516;  $\alpha_D^{20}$  +14.03.

### Action of Methyl Alcohol on $\Delta^3$ -Carene Oxide in the Presence of Sulfuric Acid.

31 g of  $\Delta^3$ -carene oxide, 20 g of methyl alcohol and 0.3 g of sulfuric acid (sp. gr. 1.84) were taken for the reaction. The carene oxide was added to the methyl

alcohol containing the sulfuric acid at such a rate that the temperature of the solution did not exceed 49°. At the conclusion of the reaction the sulfuric acid was neutralized with sodium methylate, the methyl alcohol distilled off and the residue (36 g) distilled in vacuo:

Fraction 1: 92-106° (8.5 mm); 24.5 g  $n_D^{20}$  1.4774.

Fraction 2: 106-130° (8.5 mm) 8.9 g  $n_D^{20}$  1.4818.

After a second distillation the following fractions were obtained:

Fraction 1: 96-113° (11 mm) 26.9 g  $n_D^{20}$  1.4772.

Fraction 2: 113-116° (9.5 mm) 4.7 g  $n_D^{20}$  1.4808.

Analysis of the fraction 92-113° (11 mm) for the hydroxyl group, according to Chugaev-Tserevitinov:

0.1170 g substance: v 16.2 ml; P = 750 mm (v for the blank experiment 2.81 ml).

0.1540 g substance: v 19.6 ml; t 18°.

Found %: OH 7.93, 7.59.

$C_{11}H_{20}O_2$ . Calculated %: OH 9.26.

Analysis of the 113-116° (9.5 mm) fraction for the hydroxyl group:

0.1356 g substance: v 20.3 ml; t 19°.

0.1470 g substance: v 21.3 ml; t 19° (v for the blank experiment 2.81 ml)

Found %: OH 9.07, 8.90.

$C_{11}H_{20}O_2$ . Calculated %: OH 9.26.

The 96-113° fraction (13 g) was treated with 1.2 g of boric acid. On heating the mixture for two hours in vacuo and then distilling off the portion not reacted with boric acid 1.7 g of a 90-98° (11 mm) fraction was obtained.

The boric ester remained in the flask as a very thick viscous mass. It was hydrolyzed with water with gentle heat, extracted with ether, the ether dried with potash and distilled off. On distilling the residue in vacuo 8.6 g of a fraction was obtained:

B.p. 112-112.5° (11.5 mm);  $d_4^{20}$  1.0065;  $n_D^{20}$  1.4794; MR 51.89.

$C_{11}H_{20}O_2$ . MR with a three-membered ring calculated 52.24.

Analysis for hydroxyl, according to the method of Chugaev-Tserevitinov:

0.1496 g substance; v 21.6 ml; t 17°.

0.1710 g substance: v 25.4 ml; t 14.5°; P = 756 mm.

(v for the blank experiment 2.81 ml)

Found %: OH 9.10, 9.34.

$C_{11}H_{20}O_2$ . Calculated %: OH 9.26.

Analysis for unsaturation with perphthalic acid did not show the presence of a double bond.

0.0972 g substance: 0.2544 g  $CO_2$ ; 0.0960 g  $H_2O$ .

Found %: C 71.40; H 10.98.

$C_{11}H_{20}O_2$ . Calculated %: C 71.73; H 10.87.

#### Action of Ethyl Alcohol on $\Delta^3$ -Carene Oxide in the Presence of Sulfuric Acid

20 g of  $\Delta^3$ -carene oxide, 30 g of absolute alcohol and 0.4 g of sulfuric acid were taken for the reaction. The temperature of the reaction mixture began to rise after the addition of 40% of the oxide (from 17° to 43°). The next day the sulfuric acid was neutralized with sodium ethylate. After distilling off the alcohol the residue (27 g) yielded a fraction with a b.p. of 84-117° (5 mm), 24 g.



Analysis for the hydroxyl group:

0.1928 g substance: v 25.9 ml; t 16°.

0.2160 g substance: v 28.0 ml; t 15°; P = 757.2 mm;

(v for the blank experiment 3.74 ml)

Found %: OH 8.15, 8.36.

$C_{12}H_{22}O_2$ . Calculated %: OH 8.58.

The fraction was treated with boric acid (2.5 g) under the conditions described for the experiment with methyl alcohol. The portion unreacted with boric acid had a b.p. 84-101° (6 mm) - 3 g.

After hydrolysis the boric ester yielded the following fraction upon distillation: 103-105° (6 mm) - 17.6 g.

Further fractionation yielded 16.3 g of a fraction with:

B.p. 93.5-94° (4.5 mm);  $n_D^{20}$  1.4758;  $d_4^{20}$  0.9852; MR 56.60

$C_{12}H_{22}O_2$  with a three-membered ring MR calculated: 56.86.

Analysis for the hydroxyl group:

0.2252 g substance: v 31.8 ml; t 16.5°.

0.1654 g substance: v 23.9 ml; t 15°; P = 755.6 mm.

P 755.6 mm; t 15° (v for the blank experiment 3.74 ml)

Found %: OH 8.83, 8.64.

$C_{12}H_{22}O_2$ . Calculated %: OH 8.58.

0.1132 g substance: 0.3012 g  $CO_2$ ; 0.1170 g  $H_2O$ .

Found %: C 72.59; H 11.49.

$C_{12}H_{22}O_2$ . Calculated %: C 72.66; H 11.18.

Action of n-Propyl Alcohol on  $\Delta^3$ -Carene Oxide in the Presence of Sulfuric Acid

20 g of carene oxide, 40 g of propyl alcohol and 0.4 g of sulfuric acid were taken for the reaction. Upon adding the carene oxide the temperature rose from 16° to 38°. After neutralizing with sodium propylate, distilling off the alcohol, the residue (24.6 g) was distilled in vacuo. A fraction was obtained with a b.p. of 68-120° (7 mm) - 22.5 g.

Analysis for the hydroxyl group:

0.2488 g substance: v 28.2 ml; t 16.5°.

P = 762 mm; t 15°; (v for the blank experiment 3.74 ml)

Found %: OH 7.02.

$C_{13}H_{24}O_2$ . Calculated %: OH 8.01.

After treatment with boric acid (2.1 g) and distilling off the unreacted portion (b.p. 70° at 12 mm, 106° at 5.5 mm - 3.1 g) the boric ester was hydrolyzed. After hydrolysis a fraction was obtained with b.p. 96-99° (3 mm) - 12.5 g;  $n_D^{20}$  1.4740.

A second distillation yielded: (11.8 g):

B.p. 96-98° (4 mm);  $d_4^{20}$  0.9692;  $n_D^{20}$  1.4728; MR 61.33.

$C_{13}H_{24}O_3$ . MR with a three-membered ring calculated 61.48.

Analysis for the hydroxyl group:

0.1842 g substance: v 25.0 ml; t 21.5°.

0.1492 g substance; v 20.6 ml; t 21.5°, 754.6 mm.

P = 754.6 mm; t 20° (v for the blank experiment 2.84 ml)

Found %: OH 8.33, 8.22.

$C_{13}H_{24}O_2$ . Calculated %: OH 8.01.

0.0880 g substance: 0.2362 g  $CO_2$ ; 0.0908 g  $H_2O$ .

Found %: C 73.20; H 11.46.

$C_{13}H_{24}O_2$ . Calculated %: C 73.51; H 11.40.

Action of n-Butyl Alcohol on  $\Delta^3$ -Carene Oxide in the Presence of Sulfuric Acid

20 g of carene oxide, 49 g of butyl alcohol, 0.4 g of sulfuric acid were taken. The temperature rose from 16° to 40°. Upon distillation in vacuo 21.7 g of a 60-118° (4 mm) fraction was obtained.

Analysis for the hydroxyl group:

0.2260 g substance: v 24.7 ml, t 16°.

P = 758.4 mm; t 15°; (v for the blank experiment 3.74 ml)

Found %: OH 6.59.

$C_{14}H_{26}O_2$ . Calculated %: OH 7.52.

After treatment with boric acid (10 g of the fraction and 0.8 g of boric acid were heated in vacuo for three hours. 2 g of a fraction was distilled with a b.p. of 72-120° at 5 mm) and hydrolyzing the boric acid ester, 7.3 g of a residue was obtained, which upon distillation in vacuo yielded a fraction (6.5 g):

B.p. 111-113° (4.5 mm);  $d_4^{20}$  0.9628;  $n_D^{20}$  1.4726; MR 65.78.

$C_{14}H_{26}O_2$ . MR with a three-membered ring calculated 66.10.

Analysis for the hydroxyl group:

P = 749.2 mm; (v for the blank experiment 3.74 ml).

0.1640 g substance: v 20.9 ml; t 16°.

0.2988 g substance: v 37.0 ml.

Found %: OH 7.33, 7.84.

$C_{14}H_{26}O_2$ . Calculated %: OH 7.52.

0.0794 g substance: 0.2162 g  $CO_2$ ; 0.0824 g  $H_2O$ .

Found %: C 74.25; H 11.53.

$C_{14}H_{26}O_2$ . Calculated %: C 74.27; H 11.50.

Action of Isopropyl Alcohol on Carene Oxide in the Presence of Sulfuric Acid

15 g of  $\Delta^3$ -carene oxide, 30 g of isopropyl alcohol, 0.4 g of sulfuric acid were taken. The temperature of the reaction mixture was not allowed to rise over 42°. After neutralization with sodium isopropylate and distillation in vacuo, 14.5 g of a fraction was obtained, 85-135° (11 mm).

Analysis for the hydroxyl group:

P = 750 mm; t 21° (v for the blank experiment 2.84 ml)

0.1548 g substance: v 23.9 ml; t 20°.

Found %: OH 9.40.

$C_{13}H_{24}O_2$ . Calculated %: OH 8.01.

After treating the fraction with boric acid (1.4 g) the portion unreacted with boric acid was distilled at 79-93° (7.5 mm) - 5 g. A second distillation gave the fraction 77-93° (7 mm) - 4.4 g. This fraction (3.1 g) was then distilled over sodium. A fraction was obtained with the constants:

B.p. 74-76° (5 mm);  $d_4^{20}$  0.9320;  $n_D^{20}$  1.4711; MR<sub>D</sub> 45.59.

$C_{10}H_{16}OF_1$ . Calculated MR 45.76.

According to the constants it corresponds to the aldehyde obtained by the isomerization of  $\Delta^3$ -carene oxide by zinc bromide.

Analysis of the fraction for unsaturation using perphthalic acid:

0.1204 g substance: calculated active oxygen 0.01267 g.

0.1458 g substance: calculated active oxygen 0.01534 g.

Found: 0.01134 g, 0.01392 g, or 0.89, 0.90 double bond.

0.0982 g substance: 0.2823 g  $CO_2$ ; 0.0948 g  $H_2O$ .

Found %: C 78.54; H 10.72.

$C_{10}H_{16}O$ . Calculated %: C 78.88; H 10.60.

Preparation of the Semicarbazone. 1.5 g of the fraction, 1.5 g of sodium acetate and 1 g of semicarbazide hydrochloride in an aqueous solution of methyl alcohol gave 1 g of the crude semicarbazone with a m.p. 204-217°. After recrystallization from methyl alcohol, m.p. 216-217°. After a second recrystallization the melting point did not change.

Hydrolysis of the Boric Acid Ester. The boric acid ester, remaining after distillation of the unreacted portion, was hydrolyzed. The product of the hydrolysis was extracted with ether. The ether was distilled off, the residue redistilled in vacuo. A fraction was obtained 105-118° (7 mm) - 5.5 g;  $n_D^{20}$  1.4752.

A second distillation yielded the fraction:

B.p. 104-106° (6.5 mm) - 4.2 g;  $d_4^{20}$  0.9715;  $n_D^{20}$  0.4737; MR 61.30.  
 $C_{13}H_{24}O_2$ . MR with a three membered ring calculated 61.48.

Analysis for the hydroxyl group:

P = 753.2 mm; t 23.5°; (v for the blank experiment 2.84 ml).

0.2168 g substance: v 27.5 ml; t 20.5°.

0.1890 g substance: v 25.0 ml; t 20.5°.

Found %: OH 7.78, 8.14;

$C_{13}H_{24}O_2$ . Calculated %: OH 8.01.

0.1004 g substance: 0.2694 g  $CO_2$ ; 0.1046 g  $H_2O$ .

Found %: C 73.17; H 11.57

$C_{13}H_{24}O_2$ . Calculated %: C 73.51; H 11.40.

Action of Tertiary Butyl Alcohol on  $\Delta^3$ -Carene Oxide in Presence of Sulfuric Acid

18.5 g of carene oxide, 36 g of tertiary butyl alcohol and 0.4 g of sulfuric acid were taken for the reaction. A rise in temperature was not observed on addition of the oxide. The solution was warmed to 70° for 10 minutes. At the 70° temperature of the bath the temperature inside the flask quickly rose and the alcohol began to boil. The boiling was continued for 30 minutes. After neutralization with sodium tertiary butylate the alcohol was distilled off. The residue (19 g) was distilled in vacuo. 14.6 g of a 57-78° (7 mm) fraction was obtained. After two redistillations the following fractions were obtained: 57-63° (5 mm) - 3.8 g; 63-73° (5 mm) - 7.5 g;  $n_D^{20}$  1.4725;  $d_4^{20}$  0.9340; 73-83° (5 mm) - 1.3 g.

The 2nd fraction gave a semicarbazone with a m.p. 214-216° with semicarbazide hydrochloride and sodium acetate in a medium of aqueous methyl alcohol. After recrystallization from methyl alcohol, m.p. 220-221°. A second recrystallization gave a m.p. 221-222°. Admixture with the semicarbazone of the isomerization product of carene oxide having a m.p. of 216-217° and obtained in the experiment with isopropyl alcohol, melted at 216-218°.

Analysis of the fraction 63-73° (5 mm) for unsaturation with perphthalic acid:

0.2612 g, 0.3820 g substance:  $C_{10}H_{18}O$ . calculated active oxygen 0.02749.  
0.04021 g, found 0.03019 g, 0.03248 g, or 1.1; 0.82 double bond.

Isomerization of  $\Delta^3$ -Carene Oxide in Dry Benzene by Sulfuric Acid

10 g of  $\Delta^3$ -carene oxide, 26 g of benzene and 0.7 g of sulfuric acid (sp. gr. 1.84) were taken. The carene oxide was poured into the boiling benzene containing the sulfuric acid. The reaction was accompanied by a little charring. After neutralization with sodium methylate, and distilling off the benzene, the residue (9.1 g) was distilled in vacuo. 6.7 g of a fraction with a b.p. of 52-82° (7 mm) was obtained. After three distillations the following fractions were obtained:

1) 39-62° (5 mm) - 2.4 g;  $n_D^{20}$  1.4830; 2) 62-67° (5 mm) - 3.2 g;  $d_4^{20}$  0.9331;  $n_D^{20}$  1.4726;  $MR_D$  45.62.  $C_{10}H_{16}OF_1$ . Calculated  $MR$  45.75.

Analysis for unsaturation:

0.2174 g, 0.2452 g substance:  $C_{10}H_{16}OF_1$  calculated active oxygen 0.02288 g, 0.0258 g, found 0.02145 g, 0.02247 g, or 0.93, 0.87 double bond.

The fraction with a b.p. of 62-67° (5 mm) gave a semicarbazone with a melting point of 216-217° after a second recrystallization from methyl alcohol.

#### Oxidation of $\Delta^3$ -Carene Oxide by Acetyl Hydroperoxide in Ethyl Alcohol

For the oxidation 27.5 g of  $\Delta^3$ -carene (b.p. 167-168° at 749 mm;  $n_D^{20}$  1.4720;  $d_4^{20}$  0.8647;  $\alpha_D^{20}$  +13.42°), 25.5 ml of a solution of acetyl hydroperoxide in acetic acid containing 16.67 g of the hydroperoxide (1.3 g excess), 220 ml of absolute alcohol and 0.4 g of sulfuric acid (sp. gr. 1.84) were taken. The  $\Delta^3$ -carene was poured into the alcoholic solution of the hydroperoxide containing the sulfuric acid. The temperature of the reaction mixture rose to 42°. The following day 150 ml of the alcohol was distilled off in vacuo (120 mm), the residue neutralized with a solution of potassium hydroxide and extracted with ether. The ether was dried with fused potash. A vacuum distillation gave a fraction with a b.p. of 118-138° (9 mm) - 27.4 g.

Analysis of the fraction for hydroxyl gave 9.97%;  $C_{12}H_{22}O_2$  calculated 8.58%.

18 g of the 118-138° (9 mm) fraction was treated with 2 g of boric acid by warming for 2 hours in vacuo. The unreacted portion was distilled off, 6.6 g. B.p. 116-154° (9 mm).

After hydrolysis and proceeding with the usual treatment, the boric acid ester yielded a fraction, 116-132° (8.5 mm) - 9 g.

On analysis the fraction contained 10.22% hydroxyl group;  $C_{12}H_{22}O_2$  calculated 8.58%.

Upon standing a portion of the fraction crystallized out. The crystals were separated by smearing on a porous plate. 1.8 g of crystals were obtained with a m.p. of 84-85°.

Analysis for the hydroxyl group:

$P = 757.5$  mm;  $t$  18°; (v for the blank experiment 2.84 ml).

0.0762 g substance: v 23.0 ml;  $t$  20°.

0.0762 g substance: Found %: OH 18.47.

$C_{10}H_{16}O_2$ . Calculated %: OH 20.0.

Upon removal of contained moisture by recrystallization from gasoline, crystals with a m.p. of 73-75°, corresponding in melting point and analysis to carene glycol monohydrate, were obtained.

$P = 752.8$  mm;  $t$  17°; (v for the blank experiment 2.84 ml).

0.0402 g substance: v 18.3 ml;  $t$  19.5°.

0.0372 g substance: v 17.3 ml;  $t$  19.5°.

Found %: OH 26.68, 26.88.

$C_{10}H_{20}O_3$ . Calculated %: OH 27.12.

The remaining 9 g of the initial fraction 114-138° (9 mm) and the 116-154° (9 mm) fraction were treated with 2.5 g of boric acid. The mixture was heated for 4 hours in vacuo. The portion unreacted with boric acid was distilled. B.p. 100-118° (7 mm) - 1.5 g.



After hydrolyzing the boric acid ester 7.9 g of a 107-118° (7.5 mm) fraction was obtained. After three redistillations the following fractions were separated:

- 1) 103-103.5° (6 mm) - 4 g;  $n_D^{20}$  1.4778;  $d_4^{20}$  0.9855;
- 2) 103.5-107° (6 mm) - 1.8 g;  $n_D^{20}$  1.4753.

After separating the crystals of  $\beta$ -carene glycol the following fraction was obtained on distillation of the liquid portion:

B.p. 103-104° (6 mm) - 2.3 g;  $n_D^{20}$  1.4753;  $d_4^{20}$  0.9882.

The 103-103.5° and 103-104° (6 mm) fractions were combined and redistilled. The following fraction was separated:

B.p. 103-104° (6 mm) - 5.1 g;  $d_4^{20}$  0.9855;  $n_D^{20}$  1.4753; MR 56.58  
 $C_{12}H_{22}O_2$ . MR with a three-membered ring calculated 56.86.

Analysis of the 103-104° (6 mm) fraction for the hydroxyl group:

P = 756.2 mm; t 19°; (v for the blank experiment 2.84 ml).

0.1688 g substance: v 23.0 ml, 21°.

0.1552 g substance: v 21.7 ml, 21°.

Found %: OH 8.32, 8.47.

$C_{12}H_{22}O_2$ . Calculated %: OH 8.58.

0.0962 g substance: 0.2556  $CO_2$ ; 0.0981 g  $H_2O$ .

Found %: C 72.48; H 11.38.

$C_{12}H_{22}O_2$ . Calculated %: C 72.66; H 11.18.

#### Action of Methyl Alcohol on Camphene Oxide in the Presence of Sulfuric Acid

The camphene oxide was obtained by the oxidation of camphene (b.p. 46°,  $[\alpha]_D$  in alcohol +38.5) with acetyl hydroperoxide in a solution of ether. After recrystallization from petroleum ether it had a m.p. of 86-88°;  $[\alpha]_D$  in alcohol +16.82.

25 g of camphene oxide, 33 g of methyl alcohol, 0.3 g of sulfuric acid were taken for the reaction. To 31 g of the methyl alcohol containing 0.3 g of sulfuric acid, a solution of 25 g of camphene oxide in 12 g of methyl alcohol was slowly added. The temperature of the reaction mixture rose from 16° to 52°. After neutralization with sodium methylate and distilling off the alcohol the residue was distilled in vacuo. On distillation 25 g of a 90-114° (15 mm) fraction was obtained.

Analysis for the hydroxyl group gave the hydroxyl content as 2.12%. After distilling over sodium (0.72 g) the following fractions were obtained:

- 1) 52-102° (16 mm) - 3.5 g; 2) 103-105° (16 mm) - 14.5 g.

The fraction 103-105° (16 mm) had  $n_D^{20}$  1.4654;  $d_4^{20}$  0.9760; MR found 56.07.

$C_{12}H_{22}O_2$ . Calculated MR 56.50.

0.0684 g substance: 0.1818 g  $CO_2$ ; 0.0708 g  $H_2O$ .

Found %: C 72.48; H 11.50.

$C_{12}H_{22}O_2$ . Calculated %: C 72.66; H 11.18.

After hydrolyzing the 103-105° (6 mm) fraction with 8% hydrochloric acid the product of hydrolysis was steam-distilled in vacuo at 17 mm. It solidified in the condenser. From 5 g of the fraction 1.8 g of the crystalline substance was obtained with a m.p. of 63-65°.

On treating the substance with m.p. of 63-65° with semicarbazide in an aqueous solution, adding methyl alcohol to dissolve the crystalline product, a

semicarbazone was obtained with a m.p. of 190-191°. After distilling off a 103-105° (16 mm) fraction the residue was treated with water, extracted with ether and dried with potash. After distilling off the ether, the residue (5.2 g) yielded 4.1 g of a 113-120 (14 mm) fraction upon distillation. The fraction partially crystallized. After recrystallization from methyl alcohol, m.p. 83°. A second recrystallization gave a m.p. of 84°.

0.1006 g substance: 0.2634 g CO<sub>2</sub>; 0.0990 g H<sub>2</sub>O.

Found %: C 71.40; H 10.93.

C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>. Calculated %: C 71.74; H 10.87.

Analysis for the hydroxyl group by the Chugaev-Tserevitinov method:

0.0652 g substance: v 8.2 ml (18°, 761 mm).

0.0894 g substance: v 11.0 ml (18°, 761 mm).

Found %: OH 8.96, 8.81.

C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>. Calculated %: OH 9.26.

On heating the product with a m.p. of 83° with boric acid in vacuo, a separation of water takes place. On further heating distillation of the original product does not take place. After hydrolysis of the boric acid ester the original product with a m.p. of 83° was obtained.

#### SUMMARY

1. The action of primary, secondary and tertiary alcohols on  $\Delta^3$ -carene oxide in the presence of sulfuric acid was studied.

It was shown that the primary alcohols react with the formation of the corresponding tertiary ether of carene glycol.

By the action of isopropyl alcohol, together with the formation of the isopropyl ether of carene glycol there occurs a partial isomerization to the unsaturated aldehyde, giving a semicarbazone with a m.p. of 216-218°. In the case of trimethyl carbinol the isomerization to an unsaturated aldehyde is the principal reaction.

2. An explanation was given on the difference in action of primary, secondary and tertiary alcohols on carene oxide from the point of view of their ability to form alkoxyl ions.

3. The action of methyl alcohol on camphene oxide in the presence of sulfuric acid was studied.

It was shown that the principal product is a methyl acetal of camphenilane aldehyde. Besides the acetal a tertiary methyl ether of camphene glycol was obtained.

An explanation was given for the formation of the acetal of camphenilane aldehyde and the monomethyl ether of camphene glycol.

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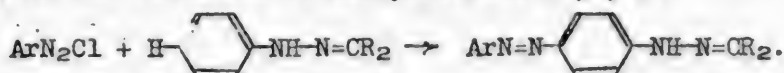
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## AZO. DERIVATIVES OF ARYL HYDRAZINES

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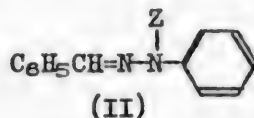
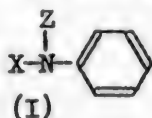
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The ability of the aryl hydrazones of aldehydes and ketones to azotize has been described in the literature, in which it was found that the azo group enters into the aryl radical of the aryl hydrazone in the para-position to the imino group with the formation of azohydrazones [1,2,3]:



Vorlander and Bittins [4] also observed such an addition with nitroaryldiazones of acetyldiphenylhydrazide.

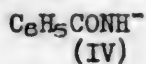
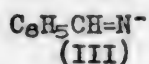
In connection with the general problem of the ability of azotization I undertook a study of the activity towards azo formation of derivatives of arylhydrazines as in formula (I):



where X is the azo-containing radical, Z = hydrogen, alkyl or phenyl. Since I had previously shown that a relationship existed between the course of azo-formation of ArX with the basicity of X [5], it was considered of interest to investigate whether a similar type of relationship also held true here. With this aim in mind I synthesized the substituents of phenylhydrazine which were described in the literature [formula (I); Z = H], methylphenylhydrazine [formula (I); Z = CH<sub>3</sub>], benzylphenylhydrazine [formula (I); Z = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>], diphenylhydrazine [formula (I); Z = C<sub>6</sub>H<sub>5</sub>], and tested their ability towards azo-formation qualitatively with the following diazones prepared on paper: 4-nitrophenyldiazonium and 2,4-dinitrophenyldiazonium. The results of these tests are given in the experimental section.

From the results obtained it must first be noted that there is a large activity in azo-formation reactions of acyl derivatives of methylphenyl hydrazine and benzylphenylhydrazine [formula (I); Z = CH<sub>3</sub>, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; X = CH<sub>3</sub>CONH, C<sub>6</sub>H<sub>5</sub>CONH] in comparison with benzalmethylphenylhydrazone [formula (II); Z = CH<sub>3</sub>] and benzalbenzylphenylhydrazone [formula (II); Z = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]. Namely, N'-benzoyl-N-methyl-N-phenylhydrazine [formula (I); Z = CH<sub>3</sub>, X = C<sub>6</sub>H<sub>5</sub>CONH] indicates an azo-formation with 2,4-dinitrophenyldiazonium as well as with 4-nitrophenyldiazonium. At the same time benzal-alkylhydrazones combine only with 2,4-dinitrophenyldiazonium, and not with 4-nitrophenyldiazonium (in the paper for five minutes). The combination of benzalalkylhydrazones with 2,4-dinitrophenyldiazonium results in compounds possessing a characteristic changing color in gaseous hydrogen chloride. The introduction of a nitrogroup into the benzaldehyde radical lowers the activity still more and, for example, 3-nitrobenzene- and 4-nitrobenzal-benzylhydrazones do not show an azo formation or indicate only a slight formation even with 2,4-dinitrophenyldiazonium. This is a very interesting result inasmuch as it is found that the benzalimino group (formula III) decreases the activity in azotization reactions

to a larger extent than the benzoylamino group (IV):



This seemed to be somewhat unexpected, since aldehyde imines (for example benzaldimine,  $\text{C}_6\text{H}_5\text{CH}=\text{NH}$ ), as their properties indicate [6], are more strongly basic than acid amides (for example benzamide,  $\text{C}_6\text{H}_5\text{CONH}_2$ ).

According to contemporary theories, the decrease in capability of azo-formation must be related to the lesser probability of the existence of compound (II) in the resonant form (V)



Since the benzalimino group (III) interferes with the formation of the resonant form (V) to a larger extent than the benzoylamino group (IV) it may be postulated that as a result of some process or other the benzalimino group combines with the free electrons of the second nitrogen atom, which possibly creates a positive charge at the nitrogen, due in all probability, to the presence of resonance.



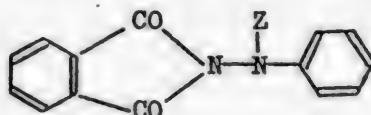
The assumption of such a resonance may explain the decrease in activity in azotization reactions with the phenyl group as well as the presence of colored arylhydrazones of aldehydes and ketones (benzalmethylphenylhydrazone is colored in contrast to the colorless benzoylmethylphenylhydrazine). It is also known that several arylhydrazones [7] are capable of azotization with the formation of formazyl compounds; it is consequently necessary to admit the presence of a negative charge at the methene group.

It is to be noted that the behavior upon azotization of arylamines of the general formula  $\text{A}=\text{N}-\text{Ar}$ , which I am studying at the present time, permits the inference of a lesser probability of the resonance:



than may be deduced from the basicity of  $\text{A}=\text{NH}$ .

In accordance with the normal basicity of the X substituents [formula (I)] phthaloyl derivatives of arylhydrazones exhibit a small activity in azotization reactions: from three compounds of the formula (VI) only N-phenylamino-phthalimide [formula (VI);  $\text{Z} = \text{H}$ ] exhibits a weak azo-formation with 2,4-dinitrophenyldiazonium; N-benzylanilino-phthalimide [formula (VI);  $\text{Z} = \text{CH}_2\text{C}_6\text{H}_5$ ] and N-diphenylamino-phthalimide [formula (VI);  $\text{Z} = \text{C}_6\text{H}_5$ ] do not exhibit azotization:





**Table 1**  
Azo Derivatives of Phenylhydrazine  $X-NH-\text{C}_6\text{H}_5$

Compound	$X^-$	$pK'_{XH}$	4-Nitrophenyldiazonium		2,4-Dinitrophenyldiazonium	
			in vapors of $C_6H_5N$	in vapors of $HCl$	in vapors of $C_6H_5N$	in vapors of $HCl$
Phenylhydrazine.....	$H_2N-$	+9.17 [9]	Formation of a diazonium compound?			
Hydrazobenzene.....	$C_6H_5NH-$	+4.6 [10]	Reduction of the diazonium			
Carbanilphenylhydrazide.....	$C_6H_5NHCONH-$	-0.3 [12]	Weak azotization			
$\beta$ -Carbethoxyphenylhydrazide....	$C_2H_5OCONH-$	>-0.8 *)			orange-yellow	orange-red
$\beta$ -Acetylphenylhydrazide.....	$CH_3CONH-$	-0.6 [11]	Weak azotization		yellow	rose-red
$\beta$ -Formylphenylhydrazide.....	$HCONH-$		weak azotization		yellow	rose-red
$\beta$ -Benzoylphenylhydrazide.....	$C_6H_5CONH-$	-1.0 [12]	weak azotization		yellow	red
$\beta$ -Acetylhydrazobenzene.....	$C_6H_5N(COCH_3)-$	-1.6 [12]	weak azotization		orange	rose-red
N-Phenylaminephthalimide.....	$C_6H_4(CO)_2N-$		very weak azotization		yellow	red
3-Nitrobenzalphenylhydrazone..	$O_2NC_6H_4CH=N-$		no azotization		very weak azotization	
4-Nitrobenzalphenylhydrazone..	$O_2NC_6H_4CH=N-$		no azotization		no azotization	

\*) Presented on the basis of the fact that urethan,  $H_2NCOOC_2H_5$ , gives a coloration with 4-dimethylaminobenzaldehyde (actual experiments).

**Table 2**  
Azo Derivatives of Methylphenylhydrazine  $X-NH-\text{C}_6\text{H}_5$

Compound	$X^-$	$pK'_{XH}$	4-Nitrophenyldiazonium		2,4-Dinitrophenyldiazonium	
			in vapors of $C_6H_5N$	in vapors of $HCl$	in vapors of $C_6H_5N$	in vapors of $HCl$
N'-Acetyl-N-methyl-N-phenylhydrazine.....	$CH_3CONH-$	-0.6 [11]	orange-yellow	Fuchsin	red	Fuchsin
N'-Benzoyl-N-methyl-N-phenylhydrazine.....	$C_6H_5CONH-$	-1.0 [12]	orange-yellow	fuchsin	red	fuchsin
Benzalmethylphenylhydrazone...	$C_6H_5CH=N-$		very weak yellow	light gray	brownish-violet	grayish-blue

**Table 3**  
Azo Derivatives of Methylphenylhydrazine  $X-N-\text{C}_6\text{H}_5$

Compound	$X^-$	$pK'_{XH}$	4-Nitrophenyldiazonium		2,4-Dinitrophenyldiazonium	
			in vapors of $C_6H_5N$	in vapors of $HCl$	in vapors of $C_6H_5N$	in vapors of $HCl$
N'-Acetyl-N-benzyl-N-phenylhydrazine.....	$CH_3CONH-$	-0.6 [11]				
N'-Benzoyl-N-benzyl-N-phenylhydrazine.....	$C_6H_5CONH-$	-1.0 [12]	yellow	violet-red	reddish-orange	fuchsin
N-benzylanilinophthalimide.....	$C_6H_4(CO)_2N-$			no azotization		
Benzalbenzylphenylhydrazone....	$C_6H_5CH=N-$		No azotization		red	violet-blue
3-Nitrobenzalbenzylphenylhydrazone.....	$O_2NC_6H_4CH=N-$			no azotization		
4-Nitrobenzalbenzylphenylhydrazone.....	$O_2N-C_6H_4CH=N-$			no azotization		

**Table 4**  
Azo Derivatives of Diphenylhydrazine  $X-N(C_6H_5)_2$

Compound	$X^-$	$pK'_{XH}$	4-Nitrophenyldiazonium		2,4-Dinitrophenyldiazonium	
			in vapors of $C_6H_5N$	in vapors of $HCl$	in vapors of $C_6H_5N$	in vapors of $HCl$
Carbethoxydiphenylhydrazine....	$C_2H_5OCONH-$	>-0.8	very weak	azotization	red	red-violet
N'-Acetyl-N,N-diphenylhydrazine	$CH_3CONH-$	-0.6 [11]	-	-	red	violet
N'-Benzoyldiphenylhydrazine....	$C_6H_5CONH-$	-1.0 [12]	-	-	red	red-violet
Formyl-diphenylhydrazine.....	$HCONH-$		very weak	azotization	red-orange	red-violet
N-Diphenylaminophthalimide....	$C_6H_4(CO)_2N-$		-	-	-	-
Benzaldiphenylhydrazone.....	$C_6H_5CH=N-$		-	-	red-violet	violet-blue
Acetophenone-diphenylhydrazone.	$C_6H_5-C(=O)-N-$		-	-	brownish red	red

As a result of the difference in conditions of azotization (limiting the time to 5 minutes and conducting the azotization with small concentrations, in our experiments), a qualitative test for azotization on paper yields somewhat different results than experiments in solutions where the action of the diazonium is prolonged. Thus, according to my experiments, acetyldiphenylhydrazide exhibits none or only a very slight azotization with 4-nitrophenyldiazonium; according to the experiments of Vorlonder and Bittins [4]; the formation is observed in acetic acid (time of azo-formation 45 minutes).

#### EXPERIMENTAL

The investigated compounds were prepared by methods described in the literature, and carefully purified; the purity of the preparation was tested by observance of the melting point. 4-Nitrophenyldiazonium was prepared on paper by application of a benzene solution of 4-nitroaniline (concentration 1 mg/ml), followed by treatment of the paper with gaseous hydrogen chloride (over hydrochloric acid sp. gr. 1.19) and then with the vapors of the alkyl nitrite [8].

2,4-Dinitrophenyldiazonium was prepared on paper by applying an alcohol-benzene solution of 2,4-dinitrophenylhydrazine (concentration 1 mg/ml) on the paper and then treating with bromine vapors; the excess bromine was blown off and the substance tested dissolved in an indifferent, easily-volatile solvent (most often in benzene) [5].

The course of azotization was observed by the appearance of a coloration; the absence of a coloration after 5 minutes was taken to indicate the absence of azotization (under these conditions). To better distinguish the color of the azotization products, it was observed in vapors of pyridine or ammonia as well as in the vapors of hydrogen chloride over hydrochloric acid sp. gr. 1.19. By changing the gaseous reagent a sharp change in the color is usually observed.

#### SUMMARY

1. The azotization of 27 derivatives of arylhydrazines was investigated.
2. Benzal-methylphenylhydrazone and benzal-benzylphenylhydrazone are less active in azotization reactions than benzoyl and acetyl derivatives of the corresponding hydrazines.
3. On the basis of the experimental material obtained a postulation was presented on the resonance of ketone hydrazones.
4. In accordance with the normal basicity of the substituents, phthaloyl derivatives of arylhydrazines exhibit little activity in azotization reactions.

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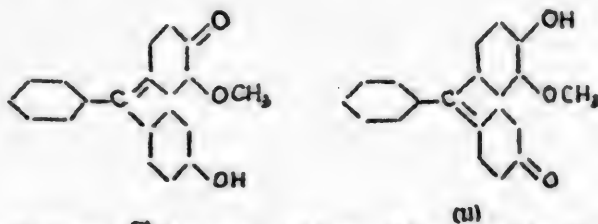
# INVESTIGATION OF HYDROXYFUCHSONE DYES

## VII (1). MONOMETHOXYBENZAURIN

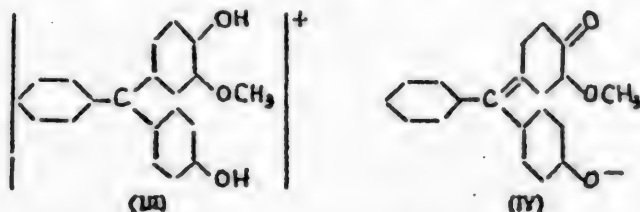
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In previous papers [1,2] the preparation and properties of several ortho-methoxy derivatives of aurin and benzaurin were described. As the missing link in our cycle of investigations, there remained monomethoxybenzaurin, for which two tautomeric forms are possible - (I) and (II).

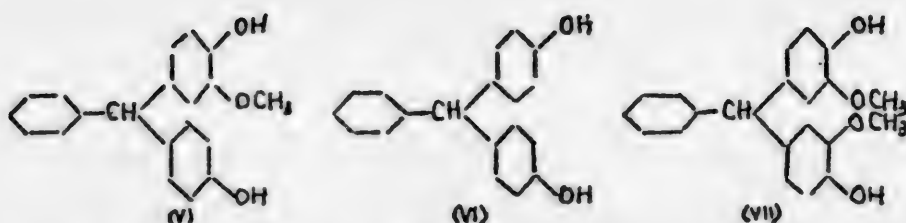


This dye, unknown up to now, attracted our attention since it should form an onium cation (III) in a mineral-acid medium, and an anion (IV) in an alkaline medium, which is an unsymmetrical structure in comparison to the corresponding ions of all the other hydroxyfuchsones we studied; this being of definite interest in theories of the color of dye materials.



However, the unsymmetrical structure of the given dye causes a certain amount of difficulty in its preparation. The simplest method seemed to be the direct preparation of the monomethoxybenzaurin by the condensation of 4-hydroxybenzophenone with guaiacol or 3-methoxy-4-hydroxybenzophenone with phenol. Experiments we conducted did not justify this expectation. We were not successful, either by warming a mixture of the benzophenone derivative with phenol in the presence of a condensing medium such as sulfuric acid, zinc chloride, etc., or by a prolonged treatment of the substances with hydrogen chloride gas. As experiments conducted by Z. Ya. Khavin, to be presented separately, indicated, the unsubstituted benzophenone in contradistinction to benzhydrale also practically did not react with phenols under these conditions.

We were therefore compelled to employ the usual method of previously preparing the corresponding leuco-derivative, 3-methoxy-4,4'-dihydroxytriphenylmethane (V) subsequently oxidizing it to the dye. But the unsymmetrical structure of the given leuco-derivative also complicated its preparation.

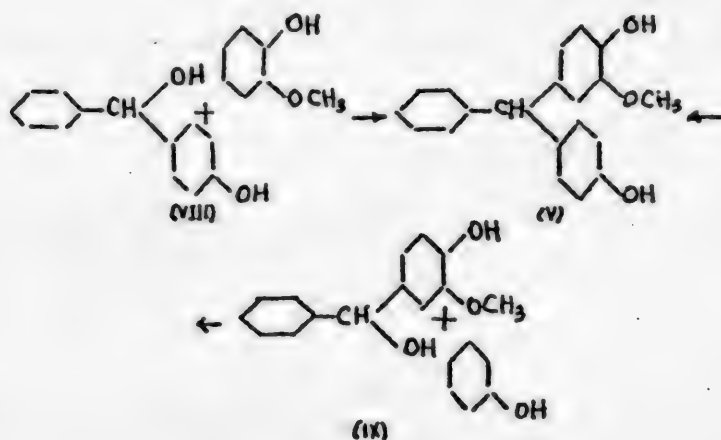


In the preparation of the symmetrical hydroxyphenylmethane derivatives, such as, for example, 4,4'-dihydroxytriphenylmethane (VI) or 3,3'-dimethoxy-4,4'-dihydroxytriphenylmethane (VII), the problem was comparatively easily solved by the condensation of benzaldehyde with an excess of the corresponding phenol, especially by employing the new method of carrying out this condensation using dry hydrogen chloride [2].

The preparation, by this means, of hydroxytriphenylmethane derivatives by the condensation of benzaldehyde and phenols evidently proceeds in two stages, both inseparable at the completion of the process; in the first stage a benzhydrol derivative is formed by the action of a mole of the aldehyde with a mole of the phenol, in the cases examined above - 4-hydroxybenzhydrol (VIII) and 3-methoxy-4-hydroxybenzhydrol (IX); in the second stage of the process the benzhydrol derivative obtained reacts with the excess phenol present, forming a symmetrical hydroxytriphenylmethane derivative.

To obtain unsymmetrical 3-methoxy-4,4'-dihydroxytriphenylmethane by this method a condensation of benzaldehyde with a mixture of phenol and guaiacol must be carried out, but in the first stage of the process both benzhydrol derivatives (VIII) and (IX) should be formed; in the second stage of the process each of these should enter into the reaction both with phenol and with guaiacol. Therefore, in the end, a mixture of three triphenylmethane derivatives should be formed - the unsymmetrical substance (V) of interest to us and the two symmetrical substances (VI) and (VII).

The problem would be easily solved if the benzhydrol derivatives (VIII) or (IX) could be first separated. In the condensation of the former with guaiacol or the latter with phenol the desired substance (V) could be formed according to the scheme:





However, hydroxybenzhydrols have to date not been obtained. There are indications in the literature that in experiments to obtain them by reduction of hydroxybenzphenones complex substances are formed, probably of the tetraphenyl-ethylene series.

We attempted to obtain such benzhydrale derivatives by the condensation of equimolecular quantities of benzaldehyde and the corresponding phenol, in particular, phenol or guaiacol. But here, instead of the sought-for hydroxybenzhydrols we obtained a hydroxytriphenylmethane derivative, unreacted benzaldehyde always remaining in the reaction medium. Notwithstanding all attempts we could not separate the above-indicated stages in the condensation of aldehydes with phenols. The reason for this may be seen from the fact that the second stage - reaction of hydroxybenzhydrol with phenol - proceeds under much more rapid conditions than the first - the formation of hydroxybenzhydrol. Therefore in the reaction of equimolecular quantities of benzaldehyde and phenol the benzhydrol derivative formed immediately enters into the reaction with the phenol present to the complete consumption of the latter. As a result a hydroxytriphenylmethane derivative is obtained, and unreacted benzaldehyde is left in the reaction medium.

After the above-described unsuccessful experiments, we were compelled, notwithstanding unfavorable theoretical prognoses, to remain with the simultaneous condensation of benzaldehyde with a mixture of phenol and guaiacol. Upon saturating a mixture of 1 mole of benzaldehyde, 1 mole of phenol and 1 mole of guaiacol with hydrogen chloride and allowing to stand for 5 days, we obtained a condensation product which proved to be a heterogeneous substance, negligibly soluble in warm benzene. The residue, washed with benzene, melted not sharply at 120-130°, and its melting point gradually increased only upon recrystallization from boiling benzene. After many recrystallizations a product was obtained with a m.p. of 160-161°, not being lowered upon admixture with known 4,4'-dihydroxytriphenylmethane.

Thus, the principal product of the condensation of 1 mole of benzaldehyde with 1 mole of phenol and 1 mole of guaiacol was 4,4'-dihydroxytriphenylmethane, contaminated with other hydroxytriphenylmethane derivatives, formed in small quantities. From this the conclusion may be drawn that phenol enters into the condensation with benzaldehyde much more quickly than guaiacol; this was found to be in agreement with our previous observations.

We therefore decided to conduct the condensation of benzaldehyde with phenol and guaiacol, using a considerable excess of the latter; we hoped that because of this, according to the laws of chemical kinetics, a considerable quantity of 3-methoxy-4-hydroxybenzhydrol (IX) would be formed in the first stage of the process together with 4-hydroxybenzhydrol (VIII), and that the 4-hydroxybenzhydrol obtained would react to a greater degree not with phenol but with guaiacol in the second stage of the process.

The experiment justified our hopes. Best results were obtained by the condensation of 1 mole of benzaldehyde with 1 mole of phenol and 5 moles of guaiacol. After saturating this mixture with dry hydrogen chloride, holding at room temperature for five days and steam-distilling off the excess guaiacol we obtained a residue in the form of an orange-colored resin, solidifying upon cooling and completely soluble in double its weight of benzene warmed to 60° (this already serves as an indication of the absence of any noticeable quantities of 4,4'-dihydroxytriphenylmethane). Upon cooling and standing, after an additional dilution with benzene, an abundant, finely-crystalline precipitate separated. After filtration and crystallization from benzene it melted at 164-166°.

A mixture of equal quantities of the substance we obtained with

4,4'-dihydroxytriphenylmethane (m.p. 161-162°) and with 3,3'-di-methoxy-4,4'-dihydroxytriphenylmethane (m.p. 147-149°) melted respectively at 140-149° and at 130-135°. Subsequent analytical determinations confirmed the fact that we actually obtained the sought-for 3-methoxy-4,4'-dihydroxytriphenylmethane. After a series of recrystallizations we were successful in raising its melting point to 168°. The acetyl derivative melted at 100-102°.

We obtained monomethoxybenzaurin as the hydrochloride salt from the 3-methoxy-4,4'-dihydroxytriphenylmethane by oxidation with amyl nitrite in amyl acetate saturated with hydrogen chloride. By conducting this reaction in very concentrated solutions, crystals of the salt partially separated and after filtration appeared as a bronze greenish-brown powder. A considerable portion of the dye still remained in the solution and was extracted from it as the bisulfite derivative. It was therefore more convenient to complete the process in more dilute solutions where all of the dye was dissolved in the amyl acetate. After washing the reaction mixture with water in a separatory funnel to remove hydrogen chloride and sodium acetate, it was repeatedly shaken with a solution of sodium bisulfite to decompose the chlorhydrate. From the combined bisulfite solutions, after the usual purification by acidification, we obtained the pure chlorhydrate of the dye, and from it - the basic dye in the hydrated form. The latter is externally very similar to the hydrated form of benzaurin and dimethoxybenzaurin. Similarly, the hydrated form of methoxybenzaurin melts not sharply below 100° and softens in hot water. The conversion of the hydrated form of monomethoxybenzaurin to the anhydro-form offered considerable difficulties. In contrast to dimethoxybenzaurin, the hydrated form of which is converted to the anhydro-form by crystallization from glacial acetic acid, monomethoxybenzaurin is too easily soluble in glacial acetic acid and does not separate even from very concentrated solutions. Destructive processes take place by the usual thermal dehydration, resulting in a contamination of the dye. Decomposition of the dye partially occurs even in attempts to crystallize it. We used the following method to prepare the anhydro form of the dye. From a solution obtained by heating the pure hydrate form with glacial acetic acid in vacuo at 70-80°, the acetic acid was distilled off together with its absorbed water. After grinding up the solid residue, it was crystallized from xylol in which the anhydro-form of the dye is soluble upon warming and almost completely insoluble at lower temperatures. The most convenient final crystallization of the anhydro-form of monomethoxybenzaurin was carried out in the following fashion: the dye was dissolved in ether, to the obtained solution was added 10% its volume of xylol and the solution was allowed to stand until the complete removal of ether was effected; in the xylol solution there then gradually grew beautifully-formed crystalline nodules of a red color with a bronze hue. These crystals darken at 150° and melt at 158-160°.

The new hydroxyfuchsone dye we obtained occupies an intermediate position between benzaurin and dimethoxybenzaurin by the color of its anion and cation. Its alkaline solutions are of a violet color, deeper than with benzaurin, but not blue as with dimethoxybenzaurin. Its acid solutions are colored a crimson-red, deeper than that of dimethoxybenzaurin.

Spectrophotometric comparisons of the dyes we obtained will be presented in one of our forthcoming papers.

#### EXPERIMENTAL

##### I. 3-Methoxy-4,4'-dihydroxytriphenylmethane

Preparation. To 53 g of benzaldehyde was added a molten mixture of 47 g of phenol and 310 g of guaiacol. While cooling the homogeneous mass so obtained with water, a stream of dry hydrogen chloride was passed through the former until saturated, after which the reaction vessel was hermetically sealed and allowed to

stand thus for five days. The reaction mixture gradually thickened and acquired a crimson color. It was poured into 0.5 liter of hot water and the excess guaiacol steam-distilled off. In the residue was obtained an orange-colored resin, solidifying upon cooling. It was separated from the water and dissolved in 300 ml of benzene warmed to 60-70°. The solution obtained was filtered and from it, after dilution with another 200 ml of benzene, the reaction product separated as a cream-colored powder, which was filtered, pressed out well on the filter paper, washed with a small quantity of benzene and then petroleum ether. After drying, 80 g of a substance was obtained with a m.p. of 154-158°. For complete purification the most convenient method was crystallization from benzene; here the reaction product was obtained as white crystals with a m.p. of 166-168°.

Properties. 3-Methoxy-4,4'-dihydroxytriphenylmethane, recrystallized from benzene, forms colorless crystals with a m.p. of 166-168°. It dissolves readily in hot benzene, poorly in cold. Soluble in the usual organic solvents. Upon exposing an alkaline solution to air it acquires a violet color.

0.1531 g substance: 0.4397 g CO<sub>2</sub>; 0.0796 g H<sub>2</sub>O.

Found %: C 78.11; H 5.76.

C<sub>20</sub>H<sub>18</sub>O<sub>3</sub>. Calculated %: C 78.43; H 5.88.

Determination of the number of hydroxyl groups by quantitative acetylation.

0.2281 g substance: 7.35 ml 0.1 N NaOH solution

Found %: OH group - 10.26.

C<sub>20</sub>H<sub>18</sub>O(OH)<sub>2</sub>. Calculated %: OH group - 10.47.

Upon dilution of the solution with water, the acetyl derivative separates as an oil, cooling to a colorless resin. Upon treating the latter with ether, it is converted to a crystalline powder. After crystallization from aqueous alcohol, colorless crystals with a m.p. of 100-102°.

## II. Methoxybenzaurin

Preparation. 30 g of 3-methoxy-4,4'-dihydroxytriphenylmethane was dissolved in 150 ml of amyl acetate. To this solution was added 100 ml of amyl acetate saturated with hydrogen chloride, and then with cooling and mixing 30 g of freshly prepared amyl nitrite was slowly added. The next day the clear-violet solution formed was shaken in a separatory funnel with 200 ml of a saturated solution of sodium acetate, and after separation of the aqueous layer, the process was repeated with water. The separated amyl acetate layer containing the methoxybenzaurin was well shaken 6 times with 50 ml of a 10% solution of sodium bisulfite, each time separating the aqueous bisulfite layer.

The combined bisulfite solutions were diluted to 500 ml with a 20% solution of sodium chloride after which animal charcoal was added, the solution filtered, and to the filtrate was added 200 ml of 15% hydrochloric acid. At this, the hydrochloride of methoxybenzaurin separated as bronze-red crystals; they were filtered, pressed out well on the filter paper, washed with a solution of acidified sodium chloride, the residue suspended in water and 50 ml of a saturated solution of sodium acetate added. The hydrated form of methoxybenzaurin, which separated as orange-red flakes, was filtered, washed well, pressed out on a porous plate and dried in a vacuum dessicator. Yield 22 g, or 70% of the theoretical.

Properties. Hydrated Form. Orange-red, finely-crystalline powder, melting not sharply at 60-80°. Softens upon addition to hot water. Soluble in alcohol, acetic acid and other solvents, giving an orange color, very similar to the color of solutions of benzaurin and dimethoxybenzaurin. Soluble in alkalis to give a violet color, which quickly decolorizes when caustic alkalis are used. It

quickly dissolves upon addition to warm bisulfite.

Chlorhydrate. Separates upon decomposing concentrated solutions of the bisulfite derivative with strong hydrochloric acid, as reddish-violet, bronzy crystals. Easily hydrolyzes, being converted to the hydrated form.

Anhydro-form. The most convenient form of preparation is dissolving the hydrated form in glacial acetic acid, followed by distillation of the acetic acid in vacuo at 70-80°. After pulverizing the dry residue, it crystallizes from xylol. Upon distilling off the ether from an ether solution, a resinous mass is obtained. If to the ether solution is added 10% of its volume of xylol and the ether slowly removed, the anhydro-form crystallizes as bronzy nodules of a red color. M.p. 158-160°, with darkening at 150°.

0.1368 g substance: 0.3947 g CO<sub>2</sub>; 0.0644 g H<sub>2</sub>O.

Found %: C 78.67; H 5.23.

C<sub>20</sub>H<sub>16</sub>O<sub>3</sub>. Calculated %: C 78.94, H 5.28.

#### SUMMARY

1. In order to obtain 3-methoxybenzaurin attempts were made to synthesize 3-methoxy-4,4'-dihydroxytriphenylmethane. These attempts met success when a mixture of 1 mole of benzaldehyde, 1 mole of phenol and 5 moles of guaiacol were saturated with dry hydrogen chloride and stored for several days. The sought-for triphenylmethane derivative was separated from the reaction medium as crystals with a m.p. of 166-168°; the acetyl derivative melts at 100-102°.

2. From the triphenylmethane derivative described, by oxidation with amyl nitrite in an amyl acetate solution, 3-methoxybenzaurin was obtained, having a low-melting hydrated form and in the anhydro-form melting at 158-160°. Alkaline solutions of this dye are colored violet; it dissolves with a crimson color in strong hydrochloric acid. In the unionized form it forms light-yellow solutions, similar to solutions of benzaurin and its dimethoxy derivative.

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## INVESTIGATION OF HYDROFUCHSONE DYES

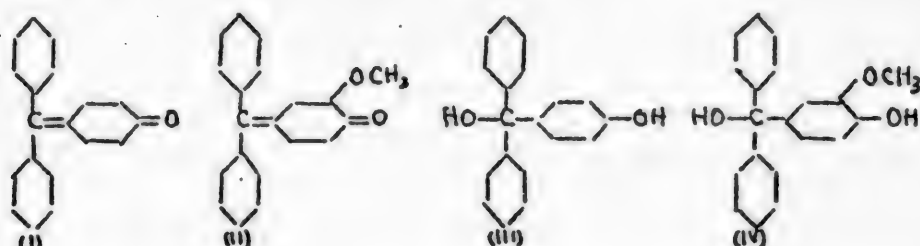
### VIII. NEW DATA ON FUCHSONE AND 3-METHOXYFUCHSONE

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For comparison with the hydroxy-methoxy-fuchsone dyes [1] studied in our laboratory, we obtained the chromogens of these dyes - fuchsone (I) and 3-methoxy-fuchsone (II).

We then succeeded in simplifying the methods for obtaining these substances and discovered some new properties not yet described in the literature.



The starting product for obtaining fuchsone is its structurally correspondent carbinol derivative, 4-hydroxy-triphenylcarbinol (III). This substance was first obtained in 1901 by Bystrzhitskii and Herbst [2] by the decarboxylation of 4-hydroxytriphenylacetic acid. Then Bystrzhitskii and Herbst tried to convert it to 4-hydroxy-triphenyl-carbinol, heating it to 70°, but this attempt failed.

It was not until 1903 [3] that Bystrzhitskii and Herbst obtained fuchsone, starting not from 4-hydroxy-triphenylcarbinol but from 4-methoxy-triphenylchloromethane, which decomposes upon heating to 180-200° with the separation of methyl chloride, forming fuchsone.

Also in 1903 Beyer and Williger [4] succeeded in accomplishing the transformation of 4-hydroxy-triphenylcarbinol into fuchsone by heating the former to 150°. To obtain fuchsone, Auvers and Schreter [5] heated 4-hydroxy-triphenylcarbinol still higher, to 200°. Thus the failure of the first experiments of Bystrzhitskii and Herbst to dehydrate 4-hydroxy-triphenylcarbinol is explained by the fact that they chose too low a reaction temperature, which was inadequate for a complete transformation of the original carbinol to fuchsone. Not until 1913 did Homberg [6] show that fuchsone may be obtained from 4-hydroxy-triphenylcarbinol at 70°, but by prolonged heating and in a current of dry air. Correspondingly, by the dehydration of 4-hydroxy-3-methoxy-triphenylcarbinol (IV), first obtained by Homberg and von-Ston [7] in 1916, 3-methoxyfuchsone (II) is obtained.

However, our experiments showed that the fuchsones formed by the thermal dehydration of hydroxy-triphenylcarbinols are subject to decomposition because

of their instability. Homberg [7] also showed that even when fuchsone is kept in a container in air, it acquires an odor of quinone as a result of an oxidative decomposition. Bystrzhitskii [8] observed an oxidative decomposition of fuchsone by evaporating its ether solutions. Homberg and von-Ston [7] found that even 3-methoxy-fuchsone is very unstable and upon heating easily decomposes with the formation of methoxy-benzoquinone. Naturally, the fuchsone and 3-methoxy-fuchsone obtained by the thermal dehydration of the corresponding hydroxytriarylcabinols were unavoidably contaminated by the products of decomposition, which made their purification very difficult.

We succeeded in finding a convenient method of preparing fuchsone and 3-methoxy fuchsones in a pure state. To accomplish this it is only necessary to boil their corresponding hydroxy-triphenylcabinols with glacial acetic acid, followed by distilling off this acid in vacuo together with the water which separated upon dehydration; the pure fuchsones are then obtained with very excellent yields.

Pure fuchsone forms clear, orange crystals with a metallic-violet cast, m.p. 167-168°. 3-Methoxy-fuchsone - light yellow crystals with a greenish cast, m.p. 180-183°. Both in an alkaline and a weakly-acid medium, both these substances easily add on water, forming the corresponding hydroxytriarylcabinols.

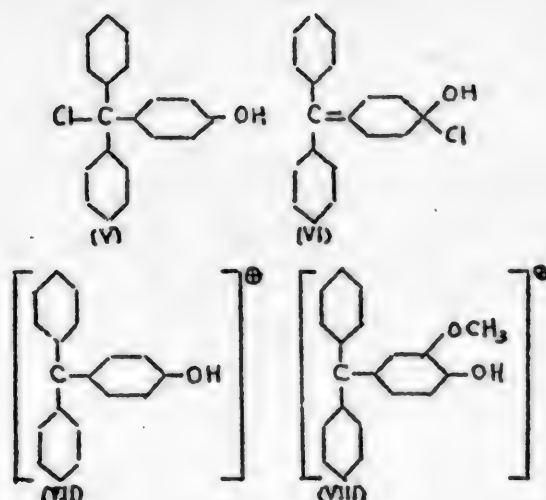
So, by reacting with alkali, fuchsone forms a colorless solution of the salt of 4-hydroxytriphenylcabinol. By means of carbon dioxide pure 4-hydroxytriphenylcabinol (III) may be precipitated from this solution, appearing as a colorless substance with a m.p. of about 165° [5].

However, the 4-hydroxy-triphenylcabinol previously obtained [2] was of a yellow color with a m.p. of 138-139°; in such a form it may be separated, for example, by boiling fuchsone with dilute acetic acid.

Thus, it seems that the formation of a colorless, high-melting or a yellow low-melting 4-hydroxy-triphenylcabinol depends on the conditions of its separation; it also seemed that each of the two forms may be converted to the other. In this connection Auvers and Schreter [5] and Bystrzhitskii and Herbst [10] proposed that this substance exists in two tautomeric (desmotropic) forms. This point of view was especially supported by Homberg's school, which obtained a series of hydroxy-triarylcabinols in the colorless as well as in the yellow form [7,11]. In particular, 4-hydroxy-3-methoxy-triphenyl cabinol was obtained [7] in the colorless form with a m.p. of 159° and in the colored with a m.p. of 147°. However, confirmation that the colorless and colored substances, formed by the hydration of fuchsones, appear as two desmotropic forms seems doubtful to us, and we will devote a special paper to this important question.

Fuchsone dissolves easily in concentrated hydrochloric or sulfuric acid and forms solutions of a yellow-brown color. Homberg described as a dark-red color the solid fuchsone chlorhydrate obtained by the action of the crystalline fuchsone with dry hydrogen chloride, but, however, did not conduct a quantitative characterization of this chlorhydrate. We found that 3-methoxy-fuchsone also dissolves in concentrated hydrochloric or sulfuric acids with the formation of red solutions. Solutions of fuchsone salts are also obtained by the action of concentrated hydrochloric or sulfuric acid on the corresponding hydroxy-triarylcabinols.

Homberg proposed that fuchsone chlorhydrate has the structure of hydroxy-triphenylchlormethane [V], existing in the tautomeric form (VI). In the light of contemporary theories it is more probable that the fuchsone salts are oniums and that the cations, (VII) for fuchsone and (VIII) for 3-methoxy-fuchsone are the color carriers.



The onium salts of fuchsones are easily hydrolyzed by water [9].

Studying the hydrolytic decomposition of the salts of fuchsone and 3-methoxyfuchsone, we encountered a new phenomenon not yet described in the literature: if to a solution of fuchsone in concentrated hydrochloric acid is carefully added ice, or the solution is well cooled externally, and a small quantity of water is added, then neither fuchsone nor 4-hydroxytriphenylcarbinol precipitates as was to be expected, but some other substance in the form of a voluminous, spongy precipitate, of a brick-red color. We filtered off this substance and dried it in a vacuum dessicator. A brick red powder was then obtained with a m.p. of 59-62. This substance is very unstable; upon washing with water or upon prolonged standing in air it is converted to the yellow 4-hydroxy-triphenylcarbinol with a m.p. of 135°.

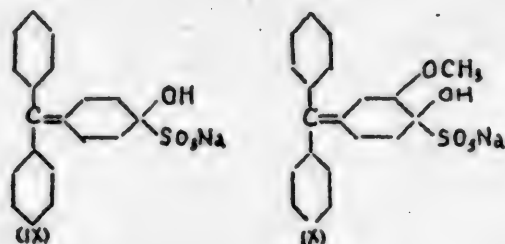
Analogously, by the decomposition with ice of the dark-red hydrochloric acid solution of 3-methoxyfuchsone, a voluminous, reddish precipitate forms, which however is so unstable that after filtration it immediately had a deliquescent action, being embedded with water; after a second filtration a yellow powder is obtained, 4-hydroxy-3-methoxy-triphenylcarbinol with a m.p. of 116-118°.

We were unable to conduct analytical determinations or to give a quantitative characterization of these new derivatives because of their instability. Inasmuch as the same substance is obtained by careful hydrolyses of sulfuric as well as hydrochloric acid solutions, we believe that these new compounds are not salts but are special hydrated forms of the fuchsones, and by analogy with the formula of Meyer and Herlofa [19] for benzaurin they may be represented as  $\text{C}_{19}\text{H}_{14}\text{O} \cdot x\text{H}_2\text{O}$  for fuchsone, and  $\text{C}_{20}\text{H}_{16}\text{O}_2 \cdot x\text{H}_2\text{O}$  for 3-methoxy-fuchsone.

In our laboratory the hydrated forms and other hydroxyfuchsone dyes were investigated [1,20,21], and it was observed that the hydrated forms of dihydroxyfuchsones are less stable than the monohydroxyfuchsones. Both of these forms are converted to the free anhydro-forms upon decomposition. Therefore the instability of the hydrated forms of the fuchsones themselves and their conversion, upon decomposition, not to the anhydro but to the carbonyl forms, are somewhat unexpected and can be explained only by the small degree of hydration of fuchsone and 3-methoxy-fuchsone.

On pouring solutions of fuchsone or 3-methoxy-fuchsone in concentrated hydrochloric or sulfuric acids into a large excess of water, the hydrated forms do not separate but the corresponding yellow colors of the hydroxy-triarylcarbinol are immediately formed.

Interesting results were obtained by comparing fuchsone and a number of its various derivatives to the bisulfite. As was indicated by Beyer and Williger [4], fuchsone forms a bisulfite derivative of the composition  $C_{19}H_{14}O \cdot NaHSO_3 \cdot 3.5H_2O$ , which according to our hypotheses [12], has the structure (IX). We obtained the bisulfite derivative of 3-methoxy-fuchsone, unknown to date, the composition of which corresponds to the formula  $C_{20}H_{18}O_2 \cdot NaHSO_3 \cdot 4H_2O$ ; it evidently has the structure (X):



Crystalline fuchsone and 3-methoxy-fuchsone enter slowly into the reaction with bisulfite even upon warming. For this purpose it is much more convenient to take alcoholic or acetic acid solutions of the fuchsones.

Beyer and Williger believed that 4-hydroxy-triphenylcarbinol also forms bisulfite derivatives; however, this is not actually so. If a solution of bisulfite acts on an alcoholic solution of colorless 4-hydroxy-triphenylcarbinol, the latter after diluting the solution with water, again separates in the crystalline form. This is especially convincing in the case of 4-hydroxy-3-methoxy-triphenylcarbinol. Only by boiling alcoholic solutions of hydroxy-triarylcarbinols with bisulfite can the formation of small quantities of bisulfite derivatives be observed, this being preceded by a preliminary dehydration of the hydroxy-triarylcarbinols to fuchsones under the influence of the high temperature of the reaction.

The bisulfite derivatives of fuchsone and 3-methoxyfuchsone are especially easily formed by the action of bisulfite with the onium salts or the above-described hydrate forms of these substances. The reaction with bisulfite is a characteristic property of the hydrate forms of fuchsone and 3-methoxy-fuchsone: in the freshly-precipitated state they instantly dissolve in the cold in bisulfite; but as soon as they are washed with water or dried in air they are converted to the yellow hydroxy-triarylcarbinols, their ability to dissolve in bisulfite then disappearing.

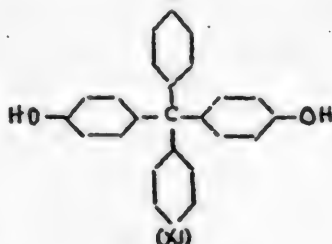
The bisulfite derivatives of fuchsone and 3-methoxy-fuchsone crystallize easily from hot water, are rather difficultly soluble in cold water. On treatment with mineral acids they decompose with the formation of solutions of onium salts of the fuchsones. From such solutions the corresponding hydroxy-triarylcarbinols may be obtained by hydrolysis and from them the fuchsones. We were able to obtain a direct reversible transformation of bisulfite derivatives to fuchsone. To accomplish this it is necessary to boil the bisulfite derivative with glacial acetic acid to the complete removal of sulfur dioxide, and then the acetic acid



is distilled off in vacuo to dryness. From the residue, containing sodium acetate and fuchsones, the latter is extracted with hot benzene and crystallized out by the addition of ether. Making use of these observations we were able considerably to simplify the methods for obtaining both hydroxy-triarylcarbinols and fuchsones.

As was already indicated, 4-hydroxy-triphenylcarbinol was first obtained by Bystrzhitskii and Herbst by the decarboxylation of 4-hydroxy-triphenylacetic acid. Beyer and Williger [4] obtained it by the demethylation of 4-methoxy-triphenylcarbinol. It was not until 1915 that Homberg and Gikling [11] worked out a new and more convenient method for obtaining 4-hydroxy-triphenylcarbinol, based on the action of benzophenone chloride with phenol, the latter in excess.

According to Homberg and Gikling, the first product of such a reaction is 4-hydroxy-triphenylchloromethane (V), which, by treatment of the reaction mixture with water and steam-distilling off the excess phenol, hydrolyzes with the formation of 4-hydroxy-triphenylcarbinol (III); as a side product 4,4'-dihydroxy-tetraphenylmethane (XI) is formed, the amount of which increases as the duration of the reaction is prolonged, and as the temperature is increased, and also depends on the ratio of the original substances:



A separation of these substances and the isolation of pure 4-hydroxy-phenylcarbinol is a very difficult operation.

We have established that 4,4'-dihydroxy-tetraphenylmethane is formed not only in the first stage of the reaction of the direct condensation of benzophenone chloride with phenol, but also during the succeeding steam-distillation of the excess phenol, when the principal product of the reaction is converted to a resinous lump, this taking place slowly as the phenol is removed, and decomposes to crystals of 4-hydroxy-triphenylcarbinol. Our experiments showed that a reaction takes place in the inside of this lump resulting in the accumulation of 4,4'-dihydroxy-tetraphenylmethane; this reaction taking place under the influence of the high temperature and under the conditions of steam distillation; this occurring still more markedly with large charges of the original substances, where the disintegration of the lump by boiling and the distillation of the phenol require a long period of time. Therefore when the operation is conducted on a large scale the yield of 4-hydroxy-triphenylcarbinol drops considerably.

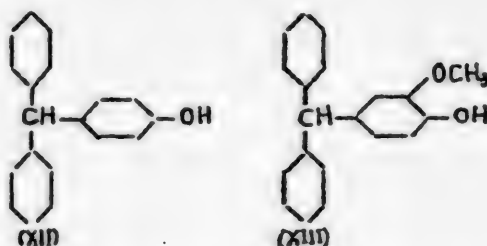
Another completion of the process, incomparably more convenient than that recommended by Homberg and Gikling, consists of the treatment of the principal reaction mixture with a warm solution of bisulfite. The bisulfite derivative thus formed is filtered and washed with benzene and ether to remove the unreacted phenol and a small quantity of benzophenone. The bisulfite derivative obtained is completely soluble in water and after recrystallization is obtained in a very pure state with a yield of over 90% of the theoretical. From the bisulfite derivative it is possible to obtain either 4-hydroxy-triphenylcarbinol, which

according to our indicated method is easily converted to fuchsone, or directly - fuchsone.

Analogously, by the condensation of benzophenone chloride with guaiacol, according to Homberg and von-Ston [7], it is possible to complete the process by the formation of a bisulfite derivative of 3-methoxy-fuchsone; this latter is converted either to 4-hydroxy-3-methoxy-triphenylcarbinol, or to 3-methoxy-fuchsone.

In the experimental section the method of Homberg and Gikling is compared with our new modification, indicating all the advantages of the latter: it is simpler to execute and gives a higher yield of the desired products. When the method of Homberg and Gikling is used, the yield of the side product - 4,4'-dihydroxy-triphenylmethane, - sometimes reaches 22% of the theoretical; in our new modification we obtained only traces of this side product and correspondingly, an increased yield of the principal substance.

Having worked out such a more convenient preparative method for obtaining hydroxy-triarylcarbinols and fuchsones, we decided to test the possibility of using for this purpose a method employed in our laboratory for the synthesis of hydroxy-fuchsone dyes and consisting of a condensation of the substances selected with the aid of dry hydrogen chloride gas. However, this type of reaction, for example a mixture of benzophenone and phenol or guaiacol, takes place unusually slowly. Under these conditions the reaction of phenols with benzhydraol takes place much more easily with the formation not of hydroxytriarylcarbinols but their corresponding leuco derivatives; in this way we obtained 4-hydroxy-triphenylmethane (XII) with a yield of about 50%:



Methods have been described in the literature for the preparation of 4-hydroxy-triphenylmethane either by the oxidation of the corresponding amino-derivative [13], or by the reduction of 4-hydroxy-triphenylcarbinol [14], or fuchsone [3], or by the condensation of diphenylbromomethane with phenol [15]; also described is the condensation of benzhydraol with phenol in the presence of  $\text{SnCl}_4$  [14] or  $\text{AlCl}_3$  [16], but in this case the yield of 4-hydroxy-triphenylmethane is very low, and the reaction product requires a complex purification. 4-Hydroxy-3-methoxy-triphenylmethane was obtained only by the reduction of the corresponding carbinol [17].

Oxidation of 4-hydroxy-triphenylmethane or 4-hydroxy-3-methoxy-triphenylmethane for the purpose of obtaining the corresponding fuchsone is not of preparative interest inasmuch as the latter are themselves unstable towards oxidizing agents, and decomposing in the process of preparation, may be separated only with very small yields. However the method we developed, consisting of the condensation of benzhydraol with phenols, is very simple, gives good yields of pure products, and we can recommend it as the most convenient method for the preparation of hydroxy-triarylmethanes.

## EXPERIMENTAL

### I. Reaction of Benzophenone Chloride with Phenols

#### 1. Reaction of Benzophenone Chloride with Phenol

80 g (4 moles) of freshly prepared phenol was melted and then cooled in a long-necked liter flask in such a way that the substance covered the wall of the flask with an even layer. To this was added in parts 48 g (1 mole) of benzophenone chloride (b.p. 174° at 15 mm); the flask was connected to a stoppered calcium chloride tube, and with slow rotation the benzophenone chloride was gradually brought into contact with the entire surface of the phenol. When the reaction mixture became homogeneous and took on the appearance of a dark, red-brown muddy oil, it was held for 15 hours at 20-25°, and then separated into two equal parts.

a) Separation of 4-Hydroxy-triphenylcarbinol according to Homberg and Gikling [11]. In the same flask the phenol was steam-distilled off from the first half of the reaction mixture. The solid residue was dissolved in 5% NaOH, and the alkaline solution obtained shaken 2 - 3 times with ether to separate the benzophenone; in order to remove the dissolved ether a strong stream of air was passed through the alkaline solution; then to the solution was added an excess of a 5 % solution of ammonium chloride. Upon this there separated a white difficultly-filterable precipitate of 4-hydroxy-triphenylcarbinol with an admixture of 4,4'-dihydroxy-tetraphenylmethane. It was filtered off, washed with water containing a few drops of ammonia and dried in a vacuum-desiccator over soda-lime. Notwithstanding every precaution, a completely colorless precipitate could not be obtained. To separate 4-hydroxy-triphenylcarbinol and dihydroxytetraphenylmethane the pulverized precipitate was treated with alcohol in the cold, 6 ml for every 1 g of the dry substance. The tetraphenylmethane derivative then remains insoluble; it was filtered off, washed with alcohol, and dried; yield 8 g, or 22% of the theoretical. To the alcoholic solution was added several drops of concentrated ammonium hydroxide; upon this, the solution almost completely decolorized, and with the addition of excess water a crystalline, yellowish precipitate of 4-hydroxy-triphenylcarbinol was separated from it. Yield 18 g, or 64% of the theoretical. This substance, which was obtained after the solution was allowed to stand one day in the cold, was treated with benzene. After filtration and washing with benzene, the almost colorless 4-hydroxy-triphenylcarbinol was obtained with a m.p. of 158-160°.

b) Separation of 4-Hydroxy-triphenylcarbinol by its Bisulfite Derivative. The second half of the reaction mixture was energetically mixed with 60 ml of a saturated solution of bisulfite, heated to 60-70°; at this point a light-yellow solution is formed, which, upon shaking with 100 ml of benzene, is converted to a thick crystalline mass of the bisulfite derivative. After standing, the precipitate was filtered off, pressed out, washed with benzene and ether, and dried. It appeared as yellowish crystals completely soluble in water. After recrystallization from hot water, with the addition of 2 - 3 ml of bisulfite solution, the bisulfite derivative was obtained as snow-white scales; yield 41 g, or 95% of the theoretical.

The benzene and ether washings were steam-distilled; in the residue 0.5 g of a resinous material was obtained, which had an odor of benzophenone and possibly contained just small traces of dihydroxy-tetraphenylmethane.

41 g of the bisulfite derivative obtained was ground in a mortar with 100-150 ml of concentrated hydrochloric acid; the next day a small sliver of ice was

added to the dark brown solution. After energetic shaking, a voluminous crimson-red precipitate of the hydrated form of fuchsone was filtered from the mother-liquor, containing sulfurous acid, pressed out and shaken up with a large quantity of water. The yellow precipitate of 4-hydroxy-triphenylcarbinol so obtained was filtered off, washed with water and dried, m.p. 135-136°. Yield 24 g, which is 90% of the theoretical according to the bisulfite derivative or 86% according to benzophenone chloride.

## 2. Reaction of Benzophenone Chloride with Guaiacol

In a long-necked, round-bottom, liter flask was mixed 192 g of benzophenone chloride (1 mole) and 240 g (2.5 moles) of freshly-prepared guaiacol. The flask was covered with a stoppered calcium chloride tube and allowed to stand at room temperature. After 3 weeks, the reaction mixture, which appeared as a dark-red, muddy viscous liquid, was separated into two equal parts.

a) Separation of 4-Hydroxy-3-methoxy-triphenylcarbinol according to Homberg and von-Ston [7]. From the first half of the reaction mixture, in the same flask, the excess guaiacol was steam-distilled off. The solid residue was ground in a mortar and dissolved in a normal solution of sodium hydroxide, and after this alkaline solution was obtained a stream of carbon dioxide gas was passed through it until complete precipitation was effected. The precipitate appeared as a voluminous, yellow, easily filterable mass. It was filtered off, shaken several times with water and again filtered; after being dried in air, the precipitate was recrystallized from hot benzene. A yellow precipitate of 4-hydroxy-3-methoxy-triphenylcarbinol then crystallized out from the yellow-brown mother liquor; yield 80 g, which was 64 % of the theoretical.

After two successive crystallizations from benzene the 4-hydroxy-3-methoxy-triphenylcarbinol appeared as colorless crystals with a m.p. of 158-159° [7].

b) Separation of 4-Hydroxy-3-methoxy-triphenylcarbinol by the Bisulfite Derivative. The second half of the reaction mixture was energetically shaken with an excess of a saturated solution of bisulfite, with warming on a water bath. A crystalline mass of the bisulfite derivative was formed, contaminated with resinous materials, excess guaiacol and probably a small quantity of benzophenone. It was shaken with a small quantity of warm water and the paste obtained was shaken with 100-150 ml of benzene. After standing, the bisulfite derivative was filtered off, pressed out, washed on the funnel with benzene and dried. After recrystallization from hot water with the addition of bisulfite solution, the bisulfite derivative appeared as snow-white scales - yield 150 g, or 80% of the theoretical. 50 g of the bisulfite derivative so obtained was dissolved in a mortar with 250 ml of concentrated hydrochloric acid. The next day the dark-red solution of 3-methoxyfuchsone chlorhydrate was hydrolyzed by the addition of a small amount of ice, and the voluminous rose-red precipitate of the hydrated form which separated was filtered off and pressed out from the mother-liquor, containing sulfurous acid. This precipitate was then shaken with a large quantity of water, and in this fashion was converted to the yellow 4-hydroxy-3-methoxy-triphenylcarbinol, which was filtered off, washed with water, and dried; m.p. 116-118°; yield 32 g, i.e. almost quantitative according to the bisulfite derivative, or 78% according to benzophenone chloride. By recrystallization from benzene the yellow 4-hydroxy-3-methoxy-triphenylcarbinol was converted to the colorless form with a m.p. of 157-159°.



## II. Preparation, Properties and Transformations of Fuchsone

### Fuchsone

#### Preparation:

##### a) Dehydration of 4-Hydroxy-triphenylcarbinol by Glacial Acetic Acid:

25 g of 4-hydroxy-triphenylcarbinol was dissolved in 125 ml of glacial acetic acid and the solution was boiled with a reflux condenser for 2 hours. Then the acetic acid plus water was distilled off in vacuo at 15 mm., the temperature of the oil bath not being higher than 90°. The residue, cooled to a glassy, brown mass, which, by means of ether, preferably by warming, was converted into a coarsely-crystalline, yellow powder of fuchsone. The latter was filtered off, washed with ether on the funnel and dried; m.p. 160-163°, yield 20 g., or 85% of the theoretical. For purification, the fuchsone was dissolved 2 - 3 times in a small quantity of benzene and recrystallized by the gradual addition of ether; it then had a melting point of 165-167° and reacted with sodium bisulfite in an alcoholic solution, leaving no residue.

b) By Decomposition of the Bisulfite Derivative: 20 g of the bisulfite derivative of fuchsone was dissolved in 100 ml of glacial acetic acid and the solution boiled in a flask with a reflux condenser for four hours on an air bath; the acetic acid was then distilled off in vacuo. The pulverized residue was first washed with warm ether, and then treated with boiling benzene. The benzene solution was filtered from the sodium acetate, evaporated to a small volume and shaken with ether. At this point the fuchsone crystallized in needles with a m.p. of 165-167°. Yield 10 g., or 83% of the theoretical.

##### Bisulfite derivative of Fuchsone.

a) The alcoholic solution of fuchsone is shaken up with a warm saturated solution of bisulfite; the mixture is diluted with a small quantity of hot water in such a way that the alcohol was approximately 50%, and warmed on a water bath until colorless. Snow-white scales of the bisulfite derivative precipitate out from the clear solution upon cooling. Under such conditions 4-hydroxy-triphenylcarbinol does not react with bisulfite.

b) Fuchsone (or 4-hydroxy-triphenylcarbinol) is dissolved by warming in a small quantity of glacial acetic acid and the solution obtained treated with an excess of a hot saturated solution of bisulfite; decolorization takes place, and on cooling a precipitate of the bisulfite derivative separates.

c) Fuchsone (or 4-hydroxy-triphenylcarbinol) is dissolved in the cold in an excess of concentrated hydrochloric acid; the brown chlorhydrate solution obtained is filtered through a glass filter and treated with such a quantity of a saturated solution of bisulfite as to neutralize all the acid. Upon standing the bisulfite derivative separates.

##### Carbinol Derivative of Fuchsone,

a) A warm alcoholic solution of fuchsone is decolorized by shaking with several drops of concentrated ammonium hydroxide; on dilution with water an almost colorless precipitate of 4-hydroxy-triphenylcarbinol separates. After filtration, washing with water, and drying, it had a m.p. of over 150°.

b) An alcoholic solution of fuchsone is boiled with an excess of normal alkali. A colorless solution is formed of the salt of 4-hydroxy-triphenylcarbinol, from which the latter is separated by the addition of a solution of ammonium chloride. The almost colorless precipitate of 4-hydroxy-triphenylcarbinol is filtered, washed with water and dried in a vacuum-desiccator over soda lime. M.p. over 150°.

c) Fuchsone is boiled with 40% acetic acid for 15-20 minutes. On cooling yellow crystals of 4-hydroxy-triphenylcarbinol separate with a m.p. of 139-140°.

d) Fuchsone is dissolved in concentrated hydrochloric acid and the solution of the chlorhydrate obtained is poured, with agitation, into an excess of water; a yellow precipitate separates of 4-hydroxy-triphenylcarbinol. Washed with water and dried, it melts at about 135°.

#### Hydrated Form of Fuchsone.

The cooled hydrochloric acid solution of fuchsone chlorhydrate, obtained either directly from fuchsone or from the bisulfite derivative, is hydrolyzed by the addition of chopped ice, with vigorous stirring; a brownish-red, voluminous, spongy precipitate of the hydrate is then formed. It is filtered off, pressed out, quickly washed with 3 N hydrochloric acid and dried in a vacuum-desiccator over calcium chloride.

The hydrated form of fuchsone is very easily soluble in bisulfite; it is a brownish-red powder with a m.p. of 59-62°. On heating in an acidic aqueous solution it melts at about 50°, being converted to dark-brown oily drops which, upon cooling, solidify into a brittle, resin-like mass; on prolonged standing with water this mass is converted to small lumps of yellow 4-hydroxy-triphenylcarbinol. The hydrated form is stable only in a strongly acid solution. It is easily converted to yellow 4-hydroxy-triphenylcarbinol (m.p. 135°) by agitation with water or by washing with water on the funnel; in the latter case a sharp decrease in volume as well as a marked heating are observed. The hydrated form is also converted to the yellow 4-hydroxy-triphenylcarbinol by exposure to air.

### 3-Methoxy-fuchsone

#### Preparation.

a) 25 g of 4-hydroxy-3-methoxy-triphenylcarbinol was boiled in a flask with a reflux condenser for 4-5 hours with 150 ml of glacial acetic acid. The acetic acid was then completely distilled off in vacuo at 15 mm and a bath temperature of about 100°. The residue then appeared as greenish-yellow crystals; it was boiled with ether, filtered off, washed with ether and dried; m.p. 180-183°; yield 20 g, or 87% of the theoretical.

b) 30 g of the bisulfite derivative of 3-methoxy-fuchsone was boiled for 4 hours in a flask with a reflux condenser with 150 ml of glacial acetic acid. After distilling the latter in vacuo the residue was pulverized, washed with ether, and then treated 2 - 3 times with boiling benzene. The 3-methoxy-fuchsone then dissolved in the benzene and the solution was separated from the sodium acetate by filtration. Upon cooling the benzene solution, which was evaporated to a small volume, pure 3-methoxy-fuchsone crystallized out. It was filtered, washed with benzene and dried; m.p. 181-183°; yield 16.5 g, or 89% of the theoretical.

#### Bisulfite Derivative of 3-Methoxy-fuchsone.

The compound is formed under the same conditions as those for the bisulfite derivative of fuchsone. It may be obtained in an alcoholic solution by the action of bisulfite only upon 3-methoxy-fuchsone; in acetic or hydrochloric acid, 4-hydroxy-3-methoxy-triphenylcarbinol may serve as the starting material. The bisulfite derivative crystallizes from aqueous solution as colorless, tiny crystals and contains 4 moles of water of crystallization.

The substance, dried to constant weight in a desiccator, was washed with several drops of concentrated nitric and sulfuric acids:

0.8702 g substance: 0.1342 g  $\text{Na}_2\text{SO}_4$   
0.9033 g substance: 0.1402 g  $\text{Na}_2\text{SO}_4$ .  
Found %: Na 4.99, 5.02.

$\text{C}_{20}\text{H}_{16}\text{O}_2 \cdot \text{NaHSO}_3 \cdot 4\text{H}_2\text{O}$ . Calculated %: Na 4.95.

Carbinol Derivative of 3-Methoxy-fuchsone. The compound is formed in the same fashion as the carbinol derivative of fuchsone. Here, by the action of ammonia or alkali on 3-methoxy-fuchsone, colorless 4-hydroxy-3-methoxy-triphenylcarbinol is formed with a m.p. of 157-159°. On boiling 3-methoxy-fuchsone with 60% acetic acid the carbinol derivative is formed, with a light-yellow color and a m.p. of 147°. On hydrolyzing the chlorhydrate of 3-methoxy-fuchsone a yellow substance with a m.p. of 116-118° is formed.

Hydrated Form of 3-Methoxy-fuchsone. A hydrochloric acid solution of 3-methoxy-fuchsone is cooled and hydrolyzed by the addition of crushed ice. Upon vigorous agitation a heavy, voluminous precipitate of the hydrate form separates, which has a dark-rose color. It may be filtered off, pressed out and quickly, by suction, washed with ice water.

The freshly-precipitated hydrated form is very easily soluble in bisulfite. Removing the dense cake of the hydrate from the filter paper, it disintegrated after drying for 10-15 minutes in a desiccator, as if it 'gave-off' water; having been filtered off and pressed out a second time, the hydrate form appeared to have lost its properties. It was converted to a yellow powder of 4-hydroxy-3-methoxy-triphenylcarbinol, insoluble in bisulfite. The former is also formed by diluting a hydrochloric acid solution of 3-methoxy-fuchsone with a large quantity of water and has a m.p. of about 116°.

### III. Condensation of Benzhydrol with Phenols

#### 4-Hydroxy-triphenylmethane

A mixture of 30 g (1 mole) of benzhydrol, 45 g (3 moles) of freshly-distilled phenol and 10 ml of glacial acetic acid was saturated, with cooling, by dry hydrogen chloride gas and held in a hermetically sealed vessel for several days. The reaction mixture was then converted to a solid mass of crystals; after steam-distilling off the excess phenol a layer of resinous material was obtained. On standing with benzene it was converted to colorless crystals of 4-hydroxy-triphenylmethane with 1 mole of benzene of crystallization [15]. These crystals were filtered from the mother-liquor, which was of a yellow color and contained resinous impurities, washed with ether, and dried. Yield 40 g, which is 73% of the theoretical. After removing the benzene of crystallization by drying at 60-70° and recrystallization from dilute acetic acid, 4-hydroxy-triphenylmethane was obtained, with a m.p. of 108-110° [14]. From it the acetyl derivative was obtained with a m.p. of 82-84°, which corresponds to the data in the literature [14].

#### 4-Hydroxy-3-methoxy-triphenylmethane

##### Preparation:

A mixture of 30 g of benzhydrol (1 mole), 100 g of freshly-distilled guaiacol (5 moles) and 15 ml of glacial acetic acid was saturated with dry hydrogen chloride and held in a hermetically sealed vessel for two weeks. Then the reaction mixture was treated as with the separation of 4-hydroxy-triphenylmethane. Yield 23 g, or 49% of the theoretical. After several crystallizations from benzene 4-hydroxy-3-methoxy-triphenylmethane was obtained with a constant m.p. of 103-105° (instead of 108°, according to data in the literature [17]). However, the 4-hydroxy-3-methoxytriphenylmethane, which we obtained by reduction of the corresponding carbinol, melted at the same temperature and was not lowered by an admixture test.

### Acetyl Derivative.

2 g of 4-hydroxy-3-methoxy-triphenylmethane, 10 g of acetic anhydride, and 0.4 g of fused sodium acetate were mixed and heated on a water bath. After 4 hours the mixture was poured into water, and on the following day the crystals of the acetate derivative which separated were filtered off, dried and twice recrystallized from alcohol; m.p. 115-116°; after several successive crystallizations they appeared as needle-shaped crystals with a m.p. of 116-118°. The yield was quantitative.

0.1525 g substance: 0.4459 g CO<sub>2</sub>; 0.0821 g H<sub>2</sub>O.

0.1523 g substance: 0.4450 g CO<sub>2</sub>; 0.0795 g H<sub>2</sub>O.

Found %: C 79.73, 79.71; H 6.02, 5.98.

C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>. Calculated %: C 79.52. H 6.02.

### SUMMARY

1. A new method has been described for the dehydration of hydroxy-triaryl carbinols, which consists of boiling these substances with glacial acetic acid, followed by distillation of the acid in vacuo. Fuchsone and 3-methoxy-fuchsone were then obtained with excellent yields and in a pure state.

2. It was established that 4,4'-dihydroxy-tetraphenylmethane, formed as a byproduct in the condensation of benzophenone chloride with phenol according to the method of Homberg and Gikling, accumulates in the reaction medium not only in the first stage of the condensation, but also in the succeeding steam-distillation of the reaction product.

3. A new and more convenient method was described for separating the corresponding hydroxy-triarylcarbinols or fuchsones from mixtures of the reaction products of benzophenone chloride with phenols. The method is based on the direct formation of the bisulfite derivatives of the fuchsones from these mixtures, followed by their decomposition.

4. It was found that by the careful hydrolysis of solutions of onium salts of fuchsones, their hydrated forms, not yet described in the literature, are obtained, and are distinguished by their instability and their conversion to the corresponding hydroxy-triarylcarbinols by drying or upon standing.

5. A new method was described for the preparation of hydroxy-triarylmethanes based on the reaction of benzhydrol with phenols in the presence of dry hydrogen chloride gas and resulting in higher yields of the final products than is known in the literature.

### LITERATURE CITED

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# ALKOXY SUBSTITUENTS OF PHOSPHOROUS ACID ESTERS AND THEIR REACTIONS WITH HALOIDO-SUBSTITUTED ETHERS

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Substituted esters of phosphorus acid have been investigated very little. Only recently Kabachnik and Rosiskaya published works on the addition of gaseous ethylene oxide to phosphorous trichloride, as a result of which the tri- $\beta$ -chloroethyl ester of phosphorous acid is obtained [1]. Previously the action of ethylene oxide on phosphorus trichloride was described in the patents of Lommel and Engelhardt [2].

The esters of monoalkyl ethers of ethylene glycol and of sulfonated carboxylic acids have been recommended as wetting agents, foaming agents, and dispersion media [3]. All the phosphorous acid esters of monoalkyl and monoaryl ethers, ethylene, propylene and butylene glycols, which may be obtained by the action of phosphorus oxychloride on the monoalkyl or monoaryl ethers of glycol, have been recommended in patents as plasticizers. [4].

A complete list of the  $\beta$ -alkoxyethyl esters of phosphorus acid has not been described in the literature. It seemed of interest to us to obtain them and to study their properties. All the phosphorous acid esters of the monomethyl ether of ethylene glycol were obtained and studied by student Dokuchaev. We obtained all the phosphorous acid esters of the monoethyl ether of ethylene glycol. The phosphorous acid esters were obtained by the method described by Milobendzki and Sachnowski [5], modified by Nikonorov; by the action of phosphorus trichloride on the monomethyl and monoethyl ethers of ethyleneglycol in a dry ether medium and in the presence of dimethylaniline. The reaction takes place according to the equation:



where R =  $CH_3$  and  $C_2H_5$ .

Tri- $\beta$ -methoxy and tri- $\beta$ -ethoxyethyl ethers of phosphorous acid are colorless, mobile liquids with odors specific for the phosphorous acid esters, but considerably weaker than the ethyl esters of phosphorous acid. The physical constants are given in Table 1.

The esters react with cuprous iodide, but the complex compounds do not crystallize.

By the action of haloido-derivatives, similar to the ester radical, the esters of phosphorous acid isomerize and are converted to derivatives of pentavalent phosphorus, as was shown and thoroughly studied by Academician A. E. Arbuzov [6]. If a small quantity is taken for the isomerization of the haloido-derivative, the reaction proceeds catalytically.

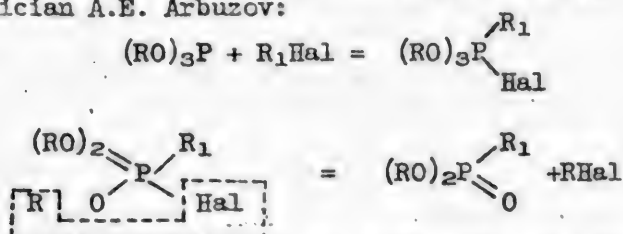
By the action of other haloido-derivatives the phosphorous acid esters are also converted to derivatives of pentavalent phosphorus; in this case the quantity of haloido-derivative required is equimolecular. Esters of haloido-substituted carboxylic acids [7], haloido-substituted ethers [8], etc., may be used as the

haloido-derivative.

TABLE 1

Formula	Boiling point	$n_D^{20}$	$d_4^{20}$	MR	
				found	calculated
$(CH_3OCH_2CH_2O)_3P$ . .	138.5-140° at 6 mm	1.4402	1.096	61.57	61.80
$(C_2H_5OCH_2CH_2O)_3P$ .	156-158° at 9 mm	1.4377	1.034	75.60	75.50

The conversion of phosphorous acid esters to derivatives of pentavalent phosphorus by the action of haloido-derivatives takes place according to the scheme of Academician A.E. Arbuzov:



We studied the isomerization of the tri-β-methoxyethyl ester of phosphorous acid by the action of methyl-α-bromomethyl ether and of the tri-β-ethoxyethyl ester of phosphorous acid by the action of β-bromodiethyl ether. The di-β-methoxyethyl ester of β-methoxyethylphosphinic acid and the di-β-ethoxyethylester of β-ethoxyethylphosphinic acid were obtained. The isomerized esters are liquids with a higher boiling point and a lower mobility than the phosphorous acid esters and are without odor. The physical constants of the isomerized esters are given in Table 2.

TABLE 2

Formula	Boiling point	$n_D^{20}$	$d_4^{20}$	MR	
				found	calculated
$(CH_3OCH_2CH_2O)_2P \begin{matrix} =O \\ \diagdown \\ CH_2CH_2OCH_3 \end{matrix}$	155-156° at 5 mm	1.4392	1.143	58.93	59.05
$(C_2H_5OCH_2CH_2O)_2P \begin{matrix} =O \\ \diagdown \\ CH_2CH_2OC_2H_5 \end{matrix}$	183-184° at 9 mm	1.4372	1.069	73.10	72.90

The isomerized esters were hydrolyzed with hydrochloric acid in sealed tubes to the corresponding alkylphosphinic acids. After evaporation, the acids remained as thick syrups, which did not crystallize on prolonged standing.

The haloido-substituted ethers react with the tri-β-methoxyethyl ester of phosphorous acid and convert it to di-β-methoxyethyl esters of alkoxymethylphosphinic acids. We studied the actions of monobromomethyl, bromomethylethyl, bromomethylpropyl ethers. The physical constants of the di-β-methoxyethyl esters of the alkoxymethylphosphinic acids are given in Table 3.

The esters obtained were hydrolyzed with hydrochloric acid. The corresponding alkoxymethylphosphinic acids were obtained as thick syrups, which did not crystallize on long standing.

The tri-β-ethoxyethyl ester of phosphorous acid also reacts with the . . .

TABLE 3

Formula	Boiling point	$n_D^{20}$	$d_4^{20}$	MR	
				Found	calculated
$(CH_3OCH_2CH_2O)_2P(=O)CH_2OCH_3$	163-164° at 13 mm	1.4375	1.1456	54.59	54.43
$(CH_3OCH_2CH_2O)_2P(=O)CH_2OC_2H_5$	168-169.5° at 13 mm	1.4373	1.1258	59.60	59.05
$(CH_3OCH_2CH_2O)_2P(=O)CH_2OC_3H_7$	157-159° at 3.5 mm	1.4389	1.101	64.43	63.67

bromo-substituents of the ethers shown above and gives the corresponding esters of alkoxymethylphosphinic acids. The physical constants of the di- $\beta$ -ethoxyethyl esters of the alkoxymethylphosphinic acids are given in Table 4.

TABLE 4

Formula	Boiling point	$n_D^{20}$	$d_4^{20}$	MR	
				Found	Calculated
$(C_2H_5OCH_2CH_2O)_2P(=O)CH_2OCH_3$	155-156° at 3.5 mm	1.4345	1.0877	64.48	63.67
$(C_2H_5OCH_2CH_2O)_2P(=O)CH_2OC_2H_5$	169-170° at 11 mm	1.4340	1.072	68.87	68.28
$(C_2H_5OCH_2CH_2O)_2P(=O)CH_2OC_3H_7$	158.5-159° at 3 mm	1.4364	1.055	73.78	72.90

The esters were hydrolyzed with hydrochloric acid. The alkoxymethylphosphinic acids are thick syrups which do not crystallize on long standing.

#### EXPERIMENTAL

##### Preparation of the Monomethyl Ether of Ethylene Glycol

The monomethyl ether of ethylene glycol was obtained from ethylene oxide with a b.p. of 12-14° and methyl alcohol, according to the directions of the German patent No. 580075 (Zbl., 1933, II, 1928). The product obtained was distilled and after two successive distillations had a b.p. of 123-125°,  $n_D^{20}$  1.4026, which corresponds to the literature data. The yield of methylcellosolve is 60% of the theoretical.

##### Preparation of the Tri- $\beta$ -methoxyethyl Ester of Phosphorous Acid

(Ester obtained by Ya. T. Dokuchaev)

The tri- $\beta$ -methoxyethyl ester of phosphorous acid was obtained according to the method of Milobendzki and Sachnowski [5], modified by Nikonorov [6], by the action of phosphorus trichloride on the monoethyl ether of ethylene glycol in the



presence of dimethylaniline.

The reaction was conducted in a round-bottom triple-necked flask with a reflux condenser, which was covered with a calcium chloride tube. The flask was fitted with a dropping funnel and a mechanical stirrer.

To a mixture of 114 g of the monomethyl ether of ethylene glycol, 182 g of freshly-distilled dimethylaniline and 350 ml of absolute alcohol was slowly added from the dropping funnel and, with rapid stirring, the phosphorous trichloride. The reaction proceeds with a great evolution of heat, so the reaction vessel was cooled with crushed ice. The hydrochloride salt of dimethylaniline quickly began to crystallize out. After all the phosphorous trichloride was added, the stirrer was operated for another half-hour. After a short period of standing, the hydrochloride of dimethylaniline was filtered off on a Buchner funnel and washed with several portions of dry ether. The ether was distilled off on a water bath and the residue distilled in vacuo. After two successive distillations the following fractions were obtained: 1) 90-134° at 5 mm, 8 g; 2) 134-137° at 5 mm, 91 g; 3) 137-145° at 5 mm, 5 g.

The desired product was found in the second fraction. After redistilling the product once more it had a b.p. of 138.5-140° at 6 mm residual pressure of mercury and the constants:  $n_D^{20}$  1.4402;  $d_4^{20}$  1.096. The yield of the ester was 71% of the theoretical.

#### Analysis for Phosphorus:

The analysis for phosphorus was conducted according to Neumann<sup>1)</sup>

0.2158 g, 0.1190 g substance:

For the titration, 41.71 ml, 22.8 ml were used of standard NaOH solution,  $T = 0.02283$  (1 ml of the solution corresponds to 0.000631 g phosphorus).

Found %: P 12.19, 12.09.

$C_9H_{21}O_6P$ . Calculated %: P 12.11.

#### Action of Cuprous Iodide on the Tri- $\beta$ -methoxyethyl Ester of Phosphorous Acid

2 g of the ester was weighed into a test tube, and after the temperature was adjusted to 17°, 1.5 g of cuprous iodide was sprinkled into it, all at once. The temperature of the reaction mixture rose to 45°. The test tube was then heated until the cuprous iodide dissolved. On cooling, the reaction product was a colorless, thick liquid, which did not crystallize on long standing.

#### Isomerization of the Phosphorous Acid Ester with Methyl- $\beta$ -bromoethyl Ether

7.4 g of tri- $\beta$ -methoxyethylphosphite and 4 g of methyl- $\beta$ -bromoethyl ether were sealed in a tube. The tube was drawn out in the middle as a fine neck in order better to observe the change in volume. The tube was heated in an oil bath at a temperature of 140-150° for 10 hours. After cooling, the volume of the reaction mass decreased and was noted. Heating a second time at the same temperature for 3 hours did not change the volume. The isomerized product was fractionated:

1) 31-150° at 10 mm, 3.5 g; 2) 150-164° at 10 mm, 6.2 g. After two successive distillations the isomerized ester was separated from the second fraction with a b.p. of 155-156.5° at 5 mm. Yield 4.5 g, or 60.8% of the theoretical.

$n_D^{20}$  1.4392;  $d_4^{20}$  1.1435; MR 58.93.

$C_9H_{21}O_6P$ . Calculated: MR 59.05.

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<sup>1)</sup>Neumann, Z. physiol., 37, 129 (1902); 43, 35 (1904)

Analysis of the ester for phosphorus:

0.1631 g substance: for the titration, 33.7 ml was used of the standard NaOH solution,  $T = 0.02085$  (1 ml of the solution corresponds to 0.0005777 g of phosphorus):

Found %: P 11.92

$C_9H_{21}O_6P$ . Calculated %: P 12.11

Hydrolysis of the Isomerized Ester

2.5 g of the di- $\beta$ -methoxyethyl ester of  $\beta$ -methoxyethylphosphinic acid and 10 ml of 10% hydrochloric acid were sealed in a tube. The tube was heated in a bath at a temperature of 130-150° for several hours. On cooling, two layers were formed. A pressure from the gases was observed on opening the tube. The top, dark brown layer was separated and added to the top layers of the other hydrolyses. The lower, clear layer was extracted with ether. The ether layer was added to the top layer. The top layer together with the top layer from the other hydrolyses and from the ether extracts of the lower layers, were fractionated after distilling off the ether. A fraction was obtained with a b.p. of 110-125°;  $n_D^{20}$  1.4020, which corresponds to the literature data for methyl cellosolve.

The lower, aqueous, clear layer was repeatedly evaporated on a water bath to the complete removal of hydrogen chloride. The residue was a thick liquid of a brownish color which did not crystallize on long standing in a vacuum-desiccator over sulfuric acid.

Action of Bromomethyl Ether on the Tri- $\beta$ -methoxyethyl Ester of Phosphorous Acid

The reaction was conducted in a round-bottom flask, fitted with a reflux condenser, covered with a calcium chloride tube, and a dropping funnel. Into the flask was placed 7 g of the tri- $\beta$ -methoxyethyl ester of phosphorous acid, and from the dropping funnel was gradually poured 3.4 g of bromomethyl ether. The reaction proceeds with little evolution of heat. The reaction mixture was then heated for 1.5 hours at 150°, after which the contents of the flask were fractionated:

- I) 21-100° at 10 mm, 2 g,  $n_D^{20}$  1.4320.
- II) 154-156° at 7 mm, 3.5 g,  $n_D^{20}$  1.4360.

After another fractionation, the second fraction had a b.p. of 163-164° at 13 mm and the constants:

$n_D^{20}$  1.4375;  $d_4^{20}$  1.1456; MR 54.59.  
 $C_8H_{19}O_6P$ . Calculated MR 54.43

Analysis for phosphorus:

0.1579 g substance: NaOH with  $T = 0.02085$ , 34.46 ml used.

Found %: P 12.59.

$C_8H_{19}O_6P$ . Calculated %: P 12.8.

Hydrolysis of the Di- $\beta$ -methoxyethyl Ester of Methoxymethylphosphinic Acid

2.2 g of di- $\beta$ -methoxyethyl ester of methoxymethylphosphinic acid and 10 ml of 10% hydrochloric acid were sealed in a tube. The tube was heated for 10 hours at 120-150°. The tube was then opened. On opening a pressure was observed. The top, brown layer was separated and added to the top layers from analogous experiments. The lower was extracted with ether. The aqueous layer was repeatedly evaporated on a water bath to the complete removal of hydrogen chloride. The residue was a thick, brownish liquid, which did not crystallize on long standing in a vacuum-desiccator over sulfuric acid.

Action of Bromoethyl Ether on the Tri- $\beta$ -methoxyethyl Ester  
of Phosphorous Acid

To 7 g of the tri- $\beta$ -methoxyethyl ester of phosphorous acid was gradually added from a dropping funnel 3.8 g of bromomethylethyl ether. The reaction mixture was then heated for 1.5 hours at 150°. The reaction products were fractionated in vacuo: I) 23-120° at 10 mm, 2.5 g; II) 160-175° at 13 mm, 4.2 g;  $n_D^{20}$  1.4360.

The second fraction, after redistillation, had a b.p. of 168-169.5° at 13 mm.

$n_D^{20}$  1.4373;  $d_4^{20}$  1.1258; MR 59.35.  
 $C_9H_{21}O_6P$ . Calculated; MR 59.05.

Analysis for phosphorus:

0.1382 g, 0.1089 g substance: NaOH solution with  $T = 0.02085$ ,  
28.5 ml, 21.84 ml used.

Found %: P 11.94, 11.60.

$C_9H_{21}O_6P$ . Calculated %: P 12.11.

Hydrolysis of the Di- $\beta$ -methoxyethyl Ester of Ethoxymethylphosphinic Acid

2.5 g of the di- $\beta$ -methoxyethyl ester of ethoxymethylphosphinic acid and 10 ml of 10% hydrochloric acid were sealed in a glass tube. The tube was heated for 10 hours at 130-150°. On opening the tube a pressure was observed. The top layer in the tube was of a brownish color; it was separated and added to the top layers of previous experiments. The lower layer, after extraction with ether, was repeatedly evaporated on a water bath to remove hydrogen chloride. The remainder was a syrupy liquid which did not crystallize on long standing in a vacuum-desiccator.

Action of Bromomethylpropyl Ether on the Tri- $\beta$ -methoxyethyl Ester  
of Phosphorous Acid

To 8 g of tri- $\beta$ -methoxyethyl ester of phosphorous acid was gradually added from a dropping funnel 5 g of bromomethylpropyl ether. The reaction mixture was then heated for 1.5 hours at 150°. The reaction product obtained was fractionated in vacuo: I) 26-130° at 10 mm, 2 g. II) 154-164° at 5 mm, 7.2 g;  $n_D^{20}$  1.4380.

The second fraction, redistilled once more, had a b.p. of 157-159° at 3.5 mm. Yield 72 % of the theoretical.

$n_D^{20}$  1.4389;  $d_4^{20}$  1.101; MR 64.43.  
 $C_{10}H_{23}O_6P$ . Calculated: MR 63.67.

Analysis for phosphorus:

0.1377 g, 0.1361 g substance: NaOH solution with  $T = 0.02085$ ,  
25.3 ml, 27.35 ml used.

Found %: P 11.43, 11.59.

$C_{10}H_{23}O_6P$ . Calculated %: P 11.48.

Preparation of the Monoethyl Ether of Ethylene Glycol

The monoethyl ether of ethylene glycol was obtained from absolute ethyl alcohol and ethylene oxide with a b.p. of 12-14° in the presence of sulfuric acid, according to German patent No. 580075 (Zbl., 1933, II, 1927). The product obtained was subjected to a fractional distillation and after two successive distillations had a b.p. of 134-135°;  $n_D^{20}$  1.4079. The yield of the monoethyl ether of ethylene glycol was 55% of the theoretical.

### Preparation of the Tri- $\beta$ -ethoxyethyl Ester of Phosphorous Acid

Into a round-bottom flask, fitted with a dropping funnel, mechanical stirrer and a reflux condenser covered with a calcium chloride tube, were placed 100 g of the monoethyl ether of ethylene glycol, 135 g of freshly-distilled dimethylaniline and 320 ml of absolute, dry ether. With rapid stirring, 51 g of phosphorus trichloride was slowly added to the mixture from the dropping funnel. The reaction flask was cooled with snow. After adding the phosphorus trichloride for an hour, the hydrochloride salt of dimethyl aniline started to crystallize out. The addition of phosphorus trichloride was continued for three hours, after which the stirrer was operated for another half-hour. After standing for a short time, the dimethylaniline hydrochloride was filtered off on a Buchner funnel and washed with several portions of dry ether. The ether was distilled off on a water bath, and the residue fractionated in vacuo. The fractions obtained were: I) 42-108° at 11 mm, 6 g; II) 120-160° at 11 mm, 97 g.

The second fraction was again fractionated and after two successive distillations had a b.p. of 156-158° at 9 mm. The yield of the ester was 83 g, or 75% of the theoretical.

$n_D^{20}$  1.4377;  $d_4^{20}$  1.034; MR 75.6.  
 $C_{12}H_{27}O_6P$ . Calculated: MR 75.5.

Analysis for phosphorus:

0.1160 g, 0.1562 g substance: NaOH solution with  $T = 0.02085$ ,  
20.7, 28.8 ml used.

Found %: P 10.30, 10.60.

$C_{12}H_{27}O_6P$ . Calculated %: P 10.40.

### Action of Cuprous Iodide on Tri- $\beta$ -ethoxyethyl Ester of Phosphorous Acid

3 g of the ester was put into the test tube and 1.9 g of cuprous iodide added. The temperature of the reaction mixture rose from 17 to 45°. The contents of the test tube were then heated until complete solution of the cuprous iodide was effected. A thick, transparent liquid was obtained which did not crystallize upon prolonged standing.

### Isomerization of the Tri- $\beta$ -ethoxyethyl Ester of Phosphorous Acid

#### with $\beta$ -Bromodiethyl Ether

8.2 g of the phosphorous acid ester and 3 g of  $\beta$ -bromodiethyl ether were sealed in a tube. The tube had a constriction for better observation of change in volume. It was heated in an oil bath at a temperature of 150-160° for 5 hours. On cooling, the change in volume was noted. A second heating for an hour did not change the volume of the ester. The contents of the tube were fractionated in vacuo: I) 30-120° at 9 mm, 2.5 g; II) 160-185° at 9 mm, 7.5 g;  $n_D^{20}$  1.4367.

The second fraction was again distilled and a product separated with a b.p. of 183-184° at 9 mm.

$n_D^{20}$  1.4372;  $d_4^{20}$  1.069; MR 73.10.  
 $C_{12}H_{27}O_6P$ . Calculated; MR 72.90.

Analysis for phosphorus:

0.1311 g, 0.1393 g substance: NaOH solution with  $T = 0.02085$ ,  
23.5 ml, 25.0 ml used up.

Found %: P 10.34, 10.33.

$C_{12}H_{27}O_6P$ . Calculated %: P 10.40.



#### Hydrolysis of Di- $\beta$ -ethoxyethyl Ester of $\beta$ -Ethoxyethylphosphinic Acid

2.2 g of the di- $\beta$ -ethoxydiethyl ester of  $\beta$ -ethoxyethylphosphinic acid and 10 ml of 10% hydrochloric acid were sealed in a tube. The tube was heated at a temperature of 140-160° for 10 hours. After being cooled, the tube was opened. On opening the tube a pressure was observed. The contents of the tube consisted of two layers: the top, oily and of a brown color, soluble as usual in ether, and the aqueous bottom layer of a light-yellow color. The top layer was separated and added to the analogous products of the other hydrolyses. Their ether solution was dried. The ether was distilled off and the residue redistilled. B.p. 105-120°;  $n_D^{20}$  1.4096. The lower layer was extracted with ether and repeatedly evaporated on the water bath to the complete removal of hydrogen chloride. The residue was a syrupy, brown liquid which did not crystallize on long standing in vacuo.

#### Action of Bromomethyl Ether on Tri- $\beta$ -ethoxyethyl Ester of Phosphorous Acid

To 8 g of the tri- $\beta$ -ethoxyethyl ester of phosphorous acid, placed in a flask, was added 3.4 g of bromomethyl ether through a dropping funnel. The reaction mixture turned a light-green color. To complete the reaction the products were heated two hours at a temperature of 150°, after which a fractionation was carried out: I) 21-50° at 6 mm, 2 g; II) 140-165° at 6 mm, 6.5 g.

The second fraction, after redistillation, had a m.p. of 155-156° at 3.5 mm.

$n_D^{20}$  1.4345;  $d_4^{20}$  1.0877; MR 64.48.

$C_{10}H_{23}O_6P$ . Calculated; MR 63.67.

Analysis for phosphorus:

0.1659 g, 0.1211 g substance: NaOH solution with T = 0.02085,  
33.4 ml, 24.3 ml used up.

Found %: P 11.60, 11.57.

$C_{10}H_{23}O_6P$ . Calculated %: P 11.31.

#### Hydrolysis of the Di- $\beta$ -ethoxyethyl Ester of Methoxymethylphosphinic Acid

2.2 g of the di- $\beta$ -ethoxyethyl ester of methoxymethylphosphinic acid was hydrolyzed with 10 ml of 10% hydrochloric acid in a sealed tube. The tube was heated for 10 hours at a temperature of 140-160°. After cooling a pressure was observed on opening the tube. The contents of the tube consisted of two layers; the separated top layer was treated as described above; the lower aqueous one was extracted several times with ether and then repeatedly evaporated on a water bath to the complete removal of hydrogen chloride. The residue was a syrupy liquid of a brown color, which did not crystallize on long standing in a vacuum-desiccator over sulfuric acid.

#### Action of Bromomethylethyl Ether on Tri- $\beta$ -ethoxyethyl Ester of Phosphorous Acid

To 8 g of the tri- $\beta$ -ethoxyethyl ester of phosphorous acid was added from a dropping funnel 3.7 g of bromomethylethyl ether. On pouring, a warming of the mixture was observed. The mixture was then warmed on an oil bath for one and a half hours at a temperature of 150-160°. The reaction products were fractionated in vacuo: I) 30-90° at 12 mm, 2.5 g.; II) 140-175° at 12 mm, 6.5 g.

The second fraction, after redistillation, had a b.p. of 169-170° at 11 mm.

$n_D^{20}$  1.4340;  $d_4^{20}$  1.072; MR 68.87.

$C_{11}H_{25}O_6P$ . Calculated: MR 68.28.

Analysis for phosphorus:

0.1175 g, 0.1640 g substance: NaOH solution with  $T = 0.02085$ ,  
22.1 ml, 30.2 ml used.

Found %: P 10.85, 11.10.

$C_{11}H_{25}O_6P$ . Calculated %: P 10.91.

Hydrolysis of the Di- $\beta$ -ethoxyethyl Ester of Ethoxymethylphosphinic Acid

1.5 g of the di- $\beta$ -ethoxyethyl ester of ethoxymethylphosphinic acid was hydrolyzed with 10 ml of 10% hydrochloric acid in a sealed tube. The tube was heated for 10 hours at a temperature of 140-160°. After cooling, a small pressure was observed on opening the tube. The contents of the tube, consisting of two layers, were separated; the top layer was treated together with those described above; the lower, aqueous one was repeatedly evaporated on a water bath. The residue was a syrupy liquid which did not crystallize on long standing in a vacuum-desiccator.

Action of Bromomethylpropyl Ether on the Tri- $\beta$ -ethoxyethyl Ester of Phosphorous Acid

To 10 g of the tri- $\beta$ -ethoxyethyl ester of phosphorous acid was added from a dropping funnel 5.1 g of bromomethylpropyl ether. The mixture was heated on an oil bath for 1.5 hours at a temperature of 150-160°. The reaction products were then fractionated in vacuo. I) 40-150° at 8 mm, 4.3 g; II) 160-175° at 8 mm, 7.7 g.

The second fraction, after redistillation, had a b.p. of 158.5-159° at 3 mm.

$n_D^{20}$  1.4364;  $d_4^{20}$  1.055; MR 73.78.

$C_{12}H_{27}O_6P$ . Calculated; MR 72.90.

Analysis for phosphorus:

0.1787 g, 0.1664 g substance: NaOH solution with  $T = 0.02085$ ,  
32 ml, 29.1 ml used up.

Found %: P 10.33, 10.10.

$C_{12}H_{27}O_6P$ . Calculated %: P 10.40.

Hydrolysis of the Di- $\beta$ -ethoxyethyl Ester of Propoxymethylphosphinic Acid

3 g of the di- $\beta$ -ethoxyethyl ester of propoxymethylphosphinic acid was hydrolyzed with 10 ml of 10% hydrochloric acid in a sealed tube. The tube was heated for 10 hours at a temperature of 140-160°. On cooling a pressure was observed on opening the tube. The top layer of the contents of the tube, after separation, was treated together with the products of the other hydrolyses; the lower aqueous layer was evaporated on a water bath to remove hydrogen chloride. The residue was a syrupy liquid, which did not crystallize after long standing in a vacuum-desiccator.

SUMMARY

1) The tri- $\beta$ -methoxyethyl and tri- $\beta$ -ethoxyethyl esters of phosphorous acid were prepared and their properties investigated.

2) The isomerization was studied of the tri- $\beta$ -methoxyethyl and tri- $\beta$ -ethoxyethyl esters of phosphorous acid by the corresponding bromo-substituted ethers to form the esters of methoxyethylphosphinic and ethoxyethylphosphinic acids.

3) The action of monobromomethyl, bromomethylethyl and bromomethylpropyl ethers on the tri- $\beta$ -methoxyethyl and tri- $\beta$ -ethoxyethyl esters of phosphorous acid was studied.

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# HYDROGENATION OF PYRIDINE HYDROCHLORIDE BASES AND THEIR MIXTURES IN THE PRESENCE OF PLATINUM BLACK. III

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The fundamental concept uniting all work on selective hydrogenation is the attempt to find the influence of the molecular structure of the hydrogenated substances on the rate and nature of their hydrogenation.

In the works of S.V. Lebedev [1], B.A.Kazanskii [2], Yu. S. Zal'kind [3], Vavon [4], Bourguet [5] and other authors [6], a series of mechanisms was established. The above-mentioned authors studied in detail the process of selective hydrogenation for ethyl and acetyl compounds.

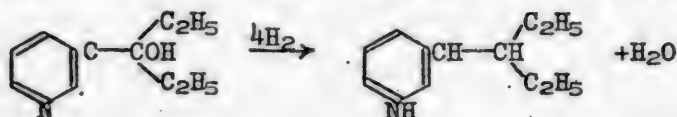
In the present paper further observations are described on the phenomenon of selective hydrogenation for a series of pyridine bases, and the influence of the structure, both as a side substituent as well as the entire molecule, on the character of hydrogenation of individual bases is shown, as well as its influence on the hydrogenation of their mixtures.

The following hydrochlorides were subjected to hydrogenation: diethyl- $\beta$ -carbinol, nicotine, anabasine and mixtures of these substances with pyridine and  $\alpha$ -picoline hydrochlorides. We conducted the hydrogenations by means of electrolytic hydrogen, shaking the solution of the hydrochlorides in absolute alcohol in a 'duck' in the presence of platinum black, prepared according to Adams. The method of operation was the same as in a previous paper, [7].

In order to obtain comparable results, we took all the components of the hydrogenation in approximately equimolecular quantities.

In the hydrogenation of the hydrochlorides of the pure individual substances, curves for the rate of their hydrogenation were obtained together with the curves for the rate of hydrogenation of pyridine hydrochloride, using one portion of the prepared catalyst (Figures 1, 2, and 3, curve I - pyridine; II - the second component).

In the hydrogenation of individual substances diethyl- $\beta$ -pyridyl-carbinol hydrochloride was of especial interest (Fig. 1, curve II). Here, instead of the 3 moles of hydrogen required for the reduction of the pyridine nucleus, 4 moles of hydrogen was absorbed. As a result of the hydrogenation a base was obtained - diethyl- $\beta$ -piperidyl, i.e. not only does a reduction of the nucleus take place, but also a substitution of hydrogen for a hydroxy group:



The question then arose as to how the hydrogenation process takes place in this molecule: whether the nucleus and the hydroxy group hydrogenate selectively or simultaneously. To clarify this question the hydrogenization was carried out up to the absorption of one molecule of hydrogen, and the products of the reaction

\*Deceased



reaction analyzed. It was established that the hydrogenation of the nucleus and the hydroxy group in diethyl- $\beta$ -piperidyl-carbinol occurs simultaneously, the amount of absorbed hydrogen being distributed in such a way that almost exactly half of it is used for the reduction of the nucleus, and the second half for the reduction of the hydroxy group. We were able to establish this fact quite accurately since the carbinol, reduced in the nucleus, gives a coloration with phenolphthalein, while the base not reduced in the nucleus does not give such a reaction; therefore, having separated the free base after absorption of one mole of hydrogen and having determined the quantity of 0.1 N hydrochloric acid used for the titration, we calculated the amount of hydrogen used up for the reduction only of the nucleus (Experiment No. 3).

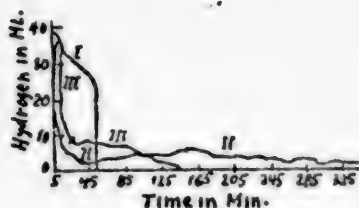


Fig. 1

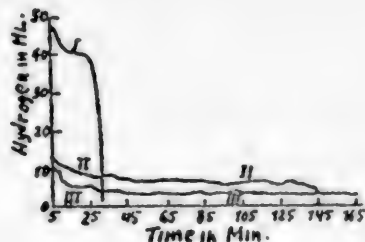


Fig. 2

In a previous paper the hydrogenation of dimethyl- $\alpha$ -picolyl-carbinol, which is also a tertiary alcohol, was described; but in this case the hydrogenation takes place normally, i.e., 3 moles of hydrogen are absorbed in the reduction with the formation of dimethyl- $\alpha$ -pipercolyl-carbinol.



The difference in the hydrogenation process of these two carbinols may evidently be explained by the fact that the hydroxy-group of diethyl- $\beta$ -pyridyl-carbinol is situated at the carbon atom connected with the nucleus ( $\alpha$ -position to the nucleus), while for dimethyl- $\alpha$ -picolyl-carbinol it is found at the farther carbon atom ( $\beta$ -position to the nucleus).

This postulation is confirmed by the work of Frank, Stroug and McElvain [8], in which  $\beta$ -ethyl-piperidyl and a small quantity of  $\beta$ -piperidyl-methyl-carbinol were obtained by the hydrogenation of  $\beta$ -acetyl pyridyl in hydrochloric acid with

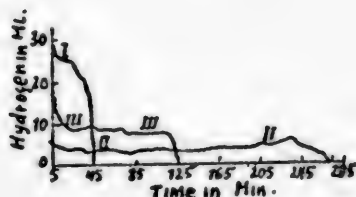


Fig. 3

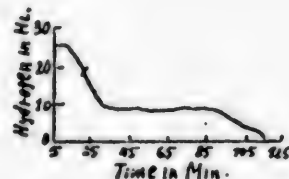


Fig. 4

platinum oxide. Evidently, the reduction process takes place in this case because the keto-group is situated next to the nucleus (in the  $\alpha$ -position to the nucleus).

Although the hydrogenation of anabasine and nicotine hydrochlorides takes place slowly, complete reduction does occur (Fig. 2 and 3, curves II, experiments 7 and 11).

In the hydrogenation of all three components in a mixture with pyridine hydrogenation curves of these mixtures were taken (Figs. 1, 2 and 3, curves III), then the hydrogenation of the mixture was carried out once more to the absorption of that quantity of hydrogen which would be necessary for the reduction of one of the components, and the mixture subjected to analysis.

On Fig 1, curve III, a sharp drop in the curve is seen where a line is shown for the theoretical quantity of hydrogen necessary for the reduction of pyridine. Indeed, analysis of the products of the interrupted hydrogenation (Experiment 5) showed that at first only pyridine hydrochloride is reduced, and even when the latter is 96% reduced the carbinol hydrochloride reaction is not impeded.

The fact that methyl- $\alpha$ -picolyl-carbinol hydrochloride hydrogenates in mixtures of pyridine hydrochloride up to 80.5%, and dimethyl- $\alpha$ -picolyl-carbinol hydrochloride up to 34% (Communication II [7]), and that diethyl- $\beta$ -pyridyl carbinol hydrochloride hydrogenates a second time in admixture with pyridine hydrochloride, evidently shows that besides the presence of a hydroxy-group as a lateral substituent in one of the components, the hydrogenation sequence of the mixture is strongly influenced by the structure of the entire molecule of the hydrogenated substance as well as the structure of the side chain containing the hydroxy group.

An examination of Figs. 2 and 3, curves III, indicates that these curves take the same course as the hydrogenation curves of the individual substances, which indicates that the components of these mixtures are simultaneously hydrogenated. Analysis of the products of the interrupted hydrogenation showed that the components of the mixtures of hydrochlorides; pyridine + anabasine and pyridine + nicotine, are simultaneously hydrogenated, the reduction in the first case being: pyridine - 38.6%, and anabasine - 61.4% (Experiment 9); in the second case pyridine 40.5% and nicotine - 59.5% (Experiment 13).

Having been convinced that several hydrochlorides of monosubstituted pyridine bases mixed with pyridine hydrochloride hydrolyze together, we decided to ascertain the course of hydrogenation of several mixtures of monosubstituted pyridine bases. Mixtures of hydrochlorides were hydrogenated:  $\alpha$ -picoline + diethyl- $\beta$ -pyridyl-carbinol,  $\alpha$ -picoline + anabasine, and  $\alpha$ -picoline + nicotine. The hydrogenation of all three mixtures occurs selectively,  $\alpha$ -picoline hydrochloride hydrogenating the first time in a mixture of  $\alpha$ -picoline + diethyl- $\beta$ -pyridyl-carbinol hydrochlorides, and on the curve for the course of hydrogenation a drop is seen, after which the curve travels almost parallel to the abscissa; at the spot where the curve breaks a line is marked to denote the theoretical quantity of hydrogen necessary for the reduction of  $\alpha$ -picoline hydrochloride (Fig. 4). By an analysis of the products of the interrupted hydrogenation of a mixture of  $\alpha$ -picoline and diethyl- $\beta$ -pyridine-carbinol hydrochlorides it was established that even when the  $\alpha$ -picoline hydrochloride is 98% reduced, the carbinol does not enter into the reaction (Experiment 14).

The course of hydrogenation of mixtures of the hydrochlorides of  $\alpha$ -picoline + anabasine and  $\alpha$ -picoline + nicotine is extremely interesting. In both mixtures the hydrogenation proceeds selectively,  $\alpha$ -picoline hydrochloride hydrogenating the second time. The curves characterizing this process are of especial interest

(Figs. 5 and 6). On both curves it is evident that the component which is first hydrogenated does so with the lowest rate of speed and only when it is completely reduced does the second component begin with a greater speed, which is expressed on the curves by sharp breaks turning upwards, the quantity of hydrogen theoretically necessary for the reduction of the hydrochlorides - in the first case (Fig. 5) anabasine; in the second case (Fig. 6) nicotine - being shown by lines.

This type of curve has been obtained to date only in the hydrogenation of phenolphthalein, the present curves having been obtained for the first time for mixtures of two substances.

Analysis of the products of the interrupted hydrogenation of these mixtures showed that the process actually does proceed selectively, and that in the first hydrogenation anabasine and nicotine are reduced (experiments 16 and 18).

From these experiments it is quite clearly shown that the hydrogenation sequence of the components in the mixture is independent of the rate of their individual hydrogenations. The rate of hydrogenation of anabasine and nicotine hydrochlorides is four times less than the rate of hydrogenation of  $\alpha$ -picoline hydrochloride, while in admixture they are strictly reduced selectively in the first hydrogenation. The character of the curves for the hydrogenation of mixtures of the hydrochlorides of  $\alpha$ -picoline + anabasine and  $\alpha$ -picoline + nicotine are one and the same; consequently, in mixtures these isomers behave analogously. It then follows that the hydrogenation sequence does not depend on whether the 6-membered piperidine ring or the 5-membered methyl-pyrrolidine ring is found in the side chain of the pyridine nucleus, and also does not depend on whether the nitrogen is secondary (anabasine) or tertiary (nicotine) in the substituent. The nature of the hydrogenation of the hydrochlorides of these substances in admixture with  $\alpha$ -picoline hydrochloride depends exclusively on the presence of the nitrogen atom in the substituent at the pyridine nucleus.

From the cases we examined we were convinced that pyridine hydrochloride, in admixture with the hydrochlorides of monosubstituted pyridine bases, does not always hydrogenate selectively. This phenomenon is observed only when there are no functional groups in the lateral substituents which would increase the absorption of this component. Indeed, we observed a strict selective hydrogenation of the mixture of two monosubstituted bases and not a simultaneous one. This indicates that a mechanical separation of the components into mono-, di-, etc., substituents cannot, in this case, answer the question of their hydrogenation sequence in admixture.

## EXPERIMENTAL

### Hydrogenation of the Hydrochlorides of:

#### Pyridine, Diethyl- $\beta$ -pyridyl-carbinol and their Mixtures

##### Experiment 1. Hydrogenation of pyridine hydrochloride.

Taken: pyridine 0.3218 g, platinum oxide 0.1990 g, HCl in alcohol 1.5 ml - 0.141 g HCl, absolute alcohol 20 ml.

T 24°, P 748 mm, p 22 mm.

A total of 317.5 ml of hydrogen was absorbed in 51 minutes (Fig. 1, curve I).

##### Experiment 2. Hydrogenation of diethyl- $\beta$ -pyridyl-carbinol.

Taken: diethyl- $\beta$ -pyridyl-carbinol 0.4118 g, platinum oxide 0.2001 g., HCl in alcohol 1 ml - 0.094 g HCl, absolute alcohol - 20 ml.

T 23°, P 736 mm, p 21 mm

Under the conditions of the experiment 232.3 ml of hydrogen is required. After 375 minutes 312 ml of hydrogen was absorbed, which corresponds to 4 moles (Fig. 1, curve II).

From the reduced product a picrate was obtained with a m.p. of 154-155°.

Analysis for nitrogen, according to Dumas:

4.682 mg substance: 10.37 ml N<sub>2</sub> (22°, 751 mm).

Found %: N 14.54.

Deviation from theoretical: 0.03%.

Experiment 3. Hydrogenation of diethyl- $\beta$ -pyridyl-carbinol hydrochloride with the purpose of explaining the reduction sequence of the hydroxy group and the nucleus.

Taken: diethyl- $\beta$ -pyridyl-carbinol 0.8300 g, platinum oxide 0.2208 g, HCl in alcohol 21 ml - 0.197 g HCl, absolute alcohol 20 ml.

T 24°, P 743 mm, p 22 mm.

By calculation, the hydrogenation was conducted to absorb one mole of hydrogen; under the conditions of the experiment 155.2 ml of hydrogen should have been absorbed. After absorption of 132 ml of hydrogen the mixture was subjected to analysis in the following fashion: the alcohol was distilled off in vacuo, the salt remaining was dissolved in a small quantity of distilled water. The solution was saturated with solid KOH, and its base extracted with petroleum ether in an extractor. After drying the ether solution the ether was distilled off and the remaining residue was dissolved in 50 ml of distilled water. On addition of phenolphthalein to the solution it acquired a red color, which indicates that a reduction of the nucleus took place in the hydrogenation. To find whether all the hydrogen was used up for the reduction of the nucleus, we titrated the solution with a 0.1 N solution of hydrochloric acid. In all, 5.3 ml of the acid was used for the titration. If only the nucleus were reduced, 10.7 ml of the acid should have been used up. Therefore, the hydrogenation of the nucleus and the hydroxy-group in diethyl- $\beta$ -pyridyl-carbinol proceeds simultaneously, half of all the absorbed hydrogen being used for the reduction of the nucleus.

Experiment 4. Hydrogenation of a mixture of pyridine and diethyl- $\beta$ -pyridyl-carbinol hydrochlorides.

Taken: pyridine 0.1028 g, diethyl- $\beta$ -pyridyl-carbinol 0.2164 g, platinum oxide 0.2012 g, HCl in alcohol 1.5 ml - 0.141 g HCl, absolute alcohol 20 ml.

T 24°, P 737 mm, p 22 mm.

After 155 minutes 241 ml of hydrogen was absorbed, (Fig. 1, curve III). For the reduction of pyridine under the conditions of the experiment, 101 ml of hydrogen is required, for the carbinol 135.9 ml of hydrogen.

Experiment 5. Interrupted hydrogenation of a mixture of the hydrochlorides of pyridine and diethyl- $\beta$ -pyridyl-carbinol.

Taken: pyridine 0.2549 g, diethyl- $\beta$ -pyridyl-carbinol 0.4007 g, platinum oxide 0.2105 g, HCl in alcohol 2.2 ml - 0.207 g HCl, absolute alcohol 20 ml.

T 26°, P 745 mm, p 24 mm.

The hydrogenation was conducted on the basis of a 96% reduction of pyridine hydrochloride. Accordingly, 240 ml of hydrogen should be absorbed. After absorption of the indicated quantity of hydrogen, the hydrogenation products were analyzed. An ether solution of the base was obtained from the decomposed hydrochloride salts, as described in experiment 3, from which, by the addition of carbon disulfide, the dithiocarbamate was separated, which melted at 168° without crystallization, i.e. at the melting point of the dithiocarbamate obtained from pure



piperidine. In all, 2.36 g of the dithiocarbamate was obtained, which is 95% of all the pyridine reduced by the absorption of hydrogen. This indicates that pyridine hydrochloride hydrogenates selectively in the case examined.

#### Hydrogenation of the Hydrochlorides of:

##### Pyridine, Anabasine and Their Mixtures

###### Experiment 6. Hydrogenation of pyridine hydrochloride.

Taken: pyridine 0.2395 g, platinum oxide 0.2012 g, HCl in alcohol 1.1 ml - 0.103 g HCl, absolute alcohol 20 ml.

T 14°, P 748 mm, p 11.7 mm.

After 29 minutes 227 ml of hydrogen was absorbed (Fig. 2, curve I).

###### Experiment 7. Hydrogenation of anabasine hydrochloride.

Taken: anabasine 0.4901 g, platinum oxide 0.2044 g, HCl in alcohol 2.4 ml - 0.225 g HCl, absolute alcohol 18 ml.

T 17°, P 740 mm, p 15 mm.

After 190 minutes 228 ml of hydrogen was absorbed (Fig. 2, curve II).

###### Experiment 8. Hydrogenation of a mixture of the hydrochlorides of pyridine and anabasine.

Taken: pyridine 0.1164 g, anabasine 0.2366 g, platinum oxide 0.2101 g, HCl in alcohol 1.8 ml - 0.169 g HCl, absolute alcohol 20 ml.

T 15°, P 731 mm, p 12.8 mm.

After 345 minutes 225.5 ml of hydrogen was absorbed (Fig. 2, curve III).

###### Experiment 9. Interrupted hydrogenation of the hydrochlorides of pyridine and anabasine.

Taken: pyridine 0.4957 g, anabasine 0.9867 g, platinum oxide 0.2926 g, HCl in alcohol 7.2 ml - 0.677 g HCl, absolute alcohol 18 ml.

T 16°, P 736 mm, p 13.6 mm.

Under the conditions of the experiment 473 ml of hydrogen is required for the complete reduction of pyridine hydrochloride; for anabasine hydrochloride - 455.1 ml of hydrogen. In all, 409 ml of hydrogen was absorbed in the hydrogenation. The solution obtained after hydrogenation was treated to obtain an ether solution of the free bases. After drying with solid KOH in vacuo at 20 mm pressure over a boiling water bath, the ether, pyridine and piperidine were distilled off. Anabasine and dipiperidine did not distill since they boil over 200°. After distilling off the bases the residue should contain anabasine and, in case it was reduced, dipiperidine. These bases were dissolved in a small quantity of distilled water and titrated with 0.1 N hydrochloric acid solution in the presence of phenolphthalein. If anabasine had not reduced at all, then 0.22 g of HCl should have been used up in its titration. Our titration took 0.343 g HCl. Therefore, the dipiperidine nucleus took 0.123 g HCl on the second reduction, or as a whole, 0.246 g HCl was used up only for the reduced anabasine, which corresponds to 0.566 g of dipiperidine, or 0.545 g of anabasine. Under the conditions of the experiment 251.2 ml of hydrogen is required for 0.545 g of anabasine. 409 ml of hydrogen was absorbed altogether. Therefore, 61.4% of all the absorbed hydrogen was spent on the reduction of anabasine. The dithiocarbamate which was obtained from the distillate had a m.p. of 167-168° (melting point of piperidine dithiocarbamate)

#### Hydrogenation of the Hydrochlorides of:

##### Pyridine, Nicotine, and their Mixtures

###### Experiment 10: Hydrogenation of pyridine hydrochloride.

Taken: pyridine 0.1981 g, platinum oxide 0.1951 g, HCl in alcohol - 1.0 ml, 0.094 g HCl, absolute alcohol 20 ml.

T 24°, P 738 mm, p 22 mm

After 45 minutes 200 ml of hydrogen was absorbed (Fig. 3, curve I).

Experiment 11. Hydrogenation of nicotine hydrochloride.

Taken: nicotine 0.4014 g, platinum oxide 0.2019 g, HCl in alcohol 2 ml - 0.188 g HCl, absolute alcohol 18 ml.

T 24°, P 738 mm, p 22 mm.

After 270 minutes 198.5 ml of hydrogen was absorbed (Fig. 3, curve II).

Experiment 12. Hydrogenation of a mixture of pyridine and nicotine hydrochlorides.

Taken: pyridine 0.1003 g, nicotine 0.2005 g, platinum oxide 0.2004 g, HCl in alcohol 1.5 ml - 0.141 g HCl, absolute alcohol 18 ml.

T 24°, P 738 mm, p 22 mm.

After 125 minutes 201 ml of hydrogen was absorbed (Fig. 3, curve III).

Experiment 13. Interrupted hydrogenation of a mixture of the hydrochlorides of pyridine and nicotine.

Taken: pyridine 0.5012 g, nicotine 0.9956 g, platinum oxide 0.2502 g, HCl in alcohol 7.2 ml - 0.677 g HCl, absolute alcohol 18 ml.

T 25°, P 739 mm, p 23 mm.

493.6 ml of hydrogen are required for the reduction of pyridine hydrochloride under the conditions of the experiment. 480.4 ml of hydrogen for nicotine hydrochloride. In all, 460 ml of hydrogen was absorbed in the hydrogenation. The solution obtained after hydrogenation was treated to obtain an ether solution of the mixture of the free bases. The ether, pyridine and piperidine were distilled off at 20 mm pressure over a boiling water bath. The residue was dissolved in 30 ml of distilled water and titrated with 0.1 N HCl. 35 ml of the acid was used, or 0.5891 g of  $\beta$ -pyrrolidine-piperidine was obtained. This consists of 0.5680 g of the original nicotine. Under the conditions of the experiment, for 0.5680 g of nicotine 274 ml of hydrogen is required, which is 57.4% of all the absorbed hydrogen. From the cooled distillate the dithiocarbamate was obtained with a m.p. of 167-168°. This indicates that only the lower-boiling fractions were distilled off.

Hydrogenation of Mixtures of  $\alpha$ -Picoline Hydrochloride with the Hydrochlorides of: Diethyl- $\beta$ -pyridyl-carbinol, Anabasine, and Nicotine

Experiment 14. Hydrogenation of a mixture of the hydrochlorides of:  $\alpha$ -picoline and diethyl- $\beta$ -pyridyl-carbinol.

Taken:  $\alpha$ -picoline 0.1188 g diethyl- $\beta$ -pyridyl-carbinol 0.2216 g, platinum oxide 0.2015 g, HCl in alcohol 1.1 ml - 0.103 g HCl, absolute alcohol 20 ml.

T 24°, P 736 mm, p 22 mm.

After 115 minutes 245 ml of hydrogen was absorbed (Fig. 4).

Experiment 15. Interrupted hydrogenation of a mixture of the hydrochlorides of  $\alpha$ -picoline and diethyl- $\beta$ -pyridyl-carbinol.

Taken:  $\alpha$ -picoline 0.2772 g, diethyl- $\beta$ -pyridyl-carbinol 0.4047 g, platinum oxide 0.2015 g, HCl in alcohol 1.1 ml - 0.103 g HCl, absolute alcohol 20 ml.

T 25°, P 745 mm, p 23 mm.

The hydrogenation was carried out on the basis of a 98% reduction of  $\alpha$ -picoline hydrochloride, for which 168 ml of hydrogen should be required. After absorption of the above amount of hydrogen, the reaction products were treated as in experiment 5. 0.269 g of the dithiocarbamate was obtained, m.p. 127-128° (melting point of pure  $\alpha$ -pipecoline dithiocarbamate), which is 94% of all the reduced  $\alpha$ -picoline.

Experiment 16. Hydrogenation of a mixture of the hydrochlorides of  $\alpha$ -picoline and anabasine.

Taken:  $\alpha$ -picoline 0.1213 g, anabasine 0.2211 g, platinum oxide 0.2016 g, HCl in alcohol 1.6 ml - 0.146 g HCl, absolute alcohol 18 ml.

T 17°, P 747 mm, p 14½ mm.

After 160 minutes 208 ml of hydrogen was absorbed (Fig. 5).

Experiment 17. Interrupted hydrogenation of a mixture of the hydrochlorides of  $\alpha$ -picoline and anabasine.

Taken:  $\alpha$ -picoline 0.2983 g, anabasine 0.6151 g, platinum oxide 0.2213 g, HCl in alcohol 4.2 ml - 0.2980 g HCl, absolute alcohol 15 ml.

T 18°, P 745 mm, p 16 mm.

As a result of the hydrogenation 245 ml of hydrogen was absorbed, which is 86.6% of the amount of hydrogen necessary for the reduction of anabasine. After decomposition of the salts and separation of the free bases, the lower-boiling fractions were distilled in vacuo, the residue in the flask was dissolved in distilled water and titrated. 70 ml of 0.1 N HCl was used up, 11 ml of 0.1 N HCl being equivalent to 0.0162 g of anabasine. Therefore, 57.9 ml of 0.1 N HCl should have been used for all the anabasine; this means that 32.1 ml of the acid was used up just for the hydrogenation of the nucleus. For all of the reduced product 64.2 ml of 0.1 N HCl was used, which corresponds to 0.5393 g of dipiperidine or 0.5200 g of the original anabasine, and is 98.3% of the anabasine entering into the reaction.

Experiment 18. Hydrogenation of a mixture of the hydrochlorides of  $\alpha$ -picoline and nicotine.

Taken:  $\alpha$ -picoline 0.1024 g, nicotine 0.2012 g, platinum oxide 0.1989 g, HCl in alcohol 1.4 ml - 0.130 g HCl, absolute alcohol 18 ml.

T 27°, P 745 mm, p 25 mm.

After 115 minutes 188.5 ml of hydrogen was absorbed (Fig. 6)

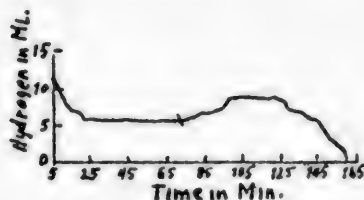


Fig. 5

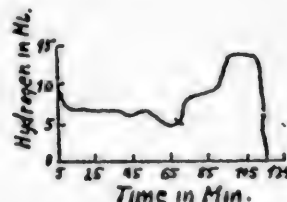


Fig. 6

Experiment 19. Interrupted hydrogenation of the hydrochlorides of  $\alpha$ -picoline and nicotine.

Taken:  $\alpha$ -picoline 0.2219 g, nicotine 0.4001 g, platinum oxide 0.2002 g, HCl in alcohol 3 ml - 0.2670 g HCl, absolute alcohol 20 ml.

In all, 180 ml of hydrogen was absorbed. After the hydrogenation, the solution was treated as in experiment 17. By titration, 0.3693 g of reduced nicotine was determined, or 95.2% of that entering into the reaction, by hydrogen absorption.

#### SUMMARY

1. The character of the hydrogenation of tertiary alcohols of the pyridine series depends on how the hydroxy-group is situated in respect to the nucleus. If the hydroxy group is found in an  $\alpha$ -position to the nucleus, the hydrogenation of the pyridine nucleus proceeds simultaneously with that of the hydroxy group; if the hydroxy group is found at the farther carbon atom, only the nucleus is hydrogenated.

2. It was shown that the hydrogenation of mixtures of pyridine hydrochloride and the hydrochlorides of mono-substituted bases does not always proceed selectively. On the other hand, a mixture of the hydrochlorides of mono-substituted bases never hydrogenates simultaneously but always selectively. These considerations are based on the structure of the molecule of the hydrogenated substances as well as on the functional groups found in the lateral substituents of the pyridine nucleus.

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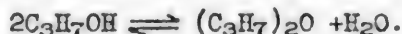
## CATALYTIC DEHYDRATION OF ISOPROPYL

### ALCOHOL TO DIISOPROPYL ETHER

A. S. Nekrasov and B. A. Krentsel

Petroleum Institute of the USSR Academy of Science

The usual method for obtaining diisopropyl ether by the reaction of isopropyl alcohol with sulfuric acid is complicated by the necessity for using considerable quantities of sulfuric acid, by the polymer-forming side reactions, and by the dehydration of the alcohol to propylene. However, of greater advantage is the steam-phase catalytic dehydration of isopropyl alcohol to diisopropyl ether, according to the following reaction:



The preparation of diisopropyl ether by such a method has been described by a series of investigations and patents [1]. In the majority of these published works there is noted a simultaneous decomposition of the isopropyl alcohol with the formation of propylene, as a result of which a substantial loss of isopropyl alcohol takes place. It would thus be of interest to select such a catalyst and such reaction conditions as would produce a higher yield of diisopropyl ether with the minimum formation of propylene.

Examining the numerous catalysts used in steam-phase dehydration reactions, we came upon alumino-silicate catalysts, which, according to available data [2], readily activate many chemical transformations, including dehydration reactions. Besides, many natural alumino-silicate catalysts are readily available, which is also of importance.

As an alumino-silicate catalyst, the ascanite clay in the vicinity of Gruzinskii, corresponding to the following chemical composition [3] was chosen:

$\text{SiO}_2$  52.58%,  $\text{Al}_2\text{O}_3$  9.18%,  $\text{Fe}_2\text{O}_3$  2.30%,  $\text{TiO}_2$  0.31%,  $\text{CaO}$  0.38%,  $\text{MgO}$  1.09%,  
 $\text{K}_2\text{O} + \text{Na}_2\text{O}$  0.43%,  $\text{H}_2\text{O}$  17.93%,  $\text{SO}_2$  0.93%.

This type of catalyst was then activated. The activated catalyst, formed in platelets of approximately 5 mm diameter (kindly prepared by A.V. Frost), was heated at a temperature of about 450° for 2-3 hours, after which it was used for the dehydration of the isopropyl alcohol.

As the starting material for the investigation a synthetic isopropyl alcohol was taken - a technical product, appearing as a clear, colorless liquid with a sharp unpleasant odor, specific gravity at 20° 0.820, coefficient of refraction  $n_D^{20}$  1.3775, and containing 82.5% of isopropyl alcohol (according to Cassar [4]).

The isopropyl alcohol was dropped at a rate of 100 ml per hour (which corresponds to 1.2 liters per hour of the alcohol per liter of catalyst) into the reaction tube filled with the catalyst (160 ml) and heated in a tubular electric furnace, fitted with a temperature regulator. After traveling through the catalyst zone the reaction products condensed in the colder portion and were collected in a vessel fitted with a reflux condenser. The uncondensed gaseous products were

collected in a gasometer.

The condensate was fractionated under a half-meter laboratory plate rectification column with a regulatory reflux. A fraction was distilled at 67-75°, corresponding to diisopropyl ether. This fraction was dried over heated calcium chloride and again distilled under the column, boiling at 67-69°, which corresponds to the boiling point of diisopropyl ether.

To obtain the pure diisopropyl ether, free even of trace admixtures of the alcohol, the triple distillate was washed with water in the ratio of 1:1, dried over solid sodium hydroxide and redistilled over metallic sodium.

#### Relationship of the Yield of the Ether Fraction to the Temperature in the Reaction Zone

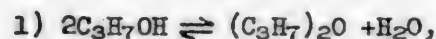
Temperature (in °C)	Yield (% by weight)
95-105	6.0
95-105	4.0
130-140	12.0
130-140	10.0
130-140	14.0
160-170	49.8
160-170	54.6
225-235	4.5

The yield of diisopropyl ether, in relationship to the temperature of the reaction, varied within the limits indicated in the table.

The data given in the table are also shown graphically in the diagram.

The decomposition of isopropyl alcohol to propylene did not take place up to 160° and at 160-170° reached 4.8% of the isopropyl alcohol passed through. At a higher temperature (240-250°) the isopropyl alcohol practically completely dehydrates to propylene, the yield of which reaches 90% of the alcohol passed over the

catalyst. This situation leads to the belief that the observation of the different investigators who studied experimentally the mechanism for the dehydration of ethyl alcohol with regard to the intermediate formation of ethyl ether, may be extended to the dehydration of isopropyl ether. In this light, the dehydration reaction of isopropyl alcohol should correspond to the following reactions:

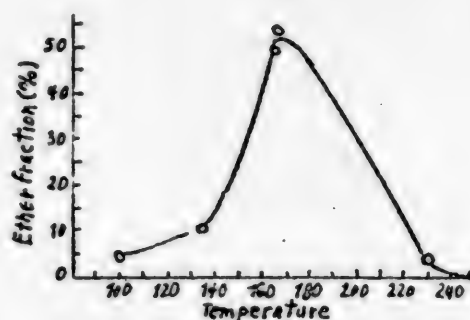


#### SUMMARY

1. The possibility was shown of dehydrating isopropyl alcohol to diisopropyl ether at a temperature of 160-170° in a steam phase over an alumino-silicate catalyst [8].

2. After one passage, the yield of the diisopropyl ether fraction reaches 40-50% of the alcohol passed through.

3. Within the temperature limits of 160-170° the dehydration of isopropyl alcohol to propylene is insignificant and is no higher than 5% of the alcohol passed over the catalyst.



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# TRANSFORMATION OF PINACOLS WITH SUBSTITUTED ACETYLENE RADICALS

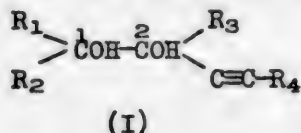
## V. SYNTHESIS AND TRANSFORMATION OF DIPHENYL-METHYL-PHENYLACETYLENYL-ETHYLENE GLYCOL E. D. Venus-Danilova, E. P. Brichko and L. A. Pavlova

Lensovet Laboratory of Organic Chemistry of the Leningrad Technological Institute

For di-tertiary  $\alpha$ -glycols having substituted acetylene radicals in the molecule, transformations in two directions may be expected.

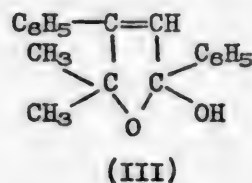
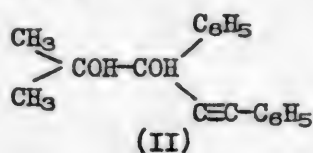
First, the special position of one of the hydroxyls - an  $\alpha$ -position with regard to the triple bond - makes possible an acetylene-allene rearrangement. Secondly, these compounds contain two tertiary alcohol groups in an  $\alpha$ -position to each other. Such a distribution in the molecules of all simple di-tertiary glycols leads, in certain conditions, to a pinacolone rearrangement, i.e., to the formation of ketones with a modified carbon skeleton.

Our previous investigation of three di-tertiary glycols [1,2,3,4] of type (I)

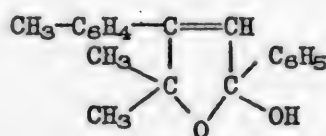
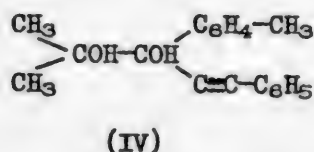


where  $R_1$  and  $R_2 = CH_3$ ;  $R_3 = C_6H_5$  or  $CH_3C_6H_4$ , and  $R_4 = C_6H_5$  or  $(CH_3)_3C$ , showed that these substances, which were first obtained by us by the catalytic action of sulfuric acid, do not dehydrate and do not form ketones, but as a result of an intra-molecular rearrangement isomerize to unsaturated  $\gamma$ -ketoalcohols, which, dependent upon the structure, may further cyclicize with the formation of substituted hydroxydihydrofurans possessing definite oxonium properties.

Thus, by the action of 30% sulfuric acid (by weight), unsym. dimethyl-phenyl-phenyl-acetylenyl-ethylene glycol (II) isomerized to a substituted hydroxyhydrofuran (III) [1]:

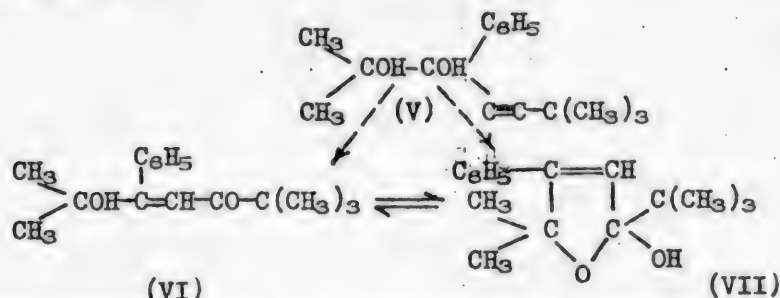


Analogously, dimethyl-p-tolyl-phenylacetylenyl-ethylene glycol (IV) is transformed, forming a substituted hydroxyhydrofuran only.





With dimethyl-phenyl-tertiarybutylacetylenyl-ethylene glycol (V) [3] there was separated, besides a substituted hydroxyhydrofuran (VII), an unsaturated  $\gamma$ -ketoalcohol (VI):

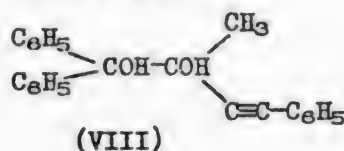


The separation of both isomeric forms - open and closed - confirmed the accuracy of one of our schemes presented for the formation of these substances according to the acetylene allene type of rearrangement [2].

A similar acetylene-allene rearrangement with the formation of an unsaturated  $\gamma$ -hydroxyaldehyde which thickens to a resinous-like product, and of small quantities of a substituted hydroxydihydrofuran having a fluorescence in acid solution, also takes place, in all probability, with phenyl-dimethyl-acetylenyl-ethylene glycol, obtained by T.A. Favorsky and A.N. Shirshov [5].

In connection with the fact that in the pinacols we investigated, only an acetylene-allene rearrangement occurred, the formation of ketones not having been observed, we considered it of interest to continue the study of similar pinacols to clarify the effect, on the nature of the glycol rearrangement, of a full or partial substitution by aromatics of the fatty radicals at the first carbon atom,  $R_1$  and  $R_2$  in Formula (I). We therefore synthesized several similar glycols and studied them in connection with sulfuric acid of different concentrations.

The transformation of diphenyl-methyl-phenylacetylenyl-ethylene glycol (VIII) is described in the present paper:



i.e., pinacol, containing two phenyl groups at the first carbon atom (Formula (I)  $R_1$  and  $R_2 = \text{C}_6\text{H}_5$ ,  $R_3 = \text{CH}_3$ .)

We synthesized this substance, according to the method of Iotzich, from diphenylacetylcarbinol (XXI) and magnesium-bromo-phenylacetylene.

The transformation of the pinacol was accomplished by heating with sulfuric acid. At first we always used 30% sulfuric acid in order to have comparative conditions, since all the previous pinacols were first treated with acid of this concentration.

Under these conditions diphenyl-methyl-phenylacetylenylethylene glycol was not changed and was almost quantitatively recovered. By the action of concentrated sulfuric acid in the cold the pinacoline rearrangement did not take place, a considerable resinification of the reaction product having been observed.

After a series of experiments we found suitable conditions: by heating with 40% sulfuric acid a single, individual product was obtained, differing from the

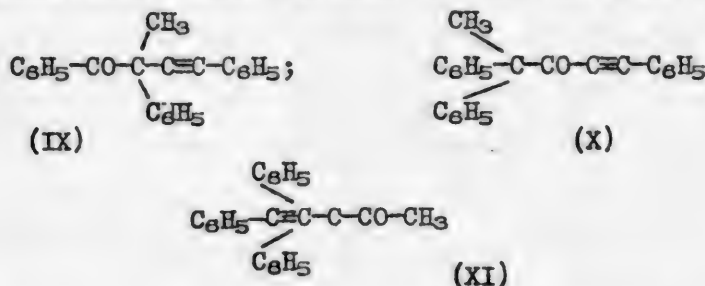
original glycol. Analysis showed that this substance was obtained with the separation of one molecule of water from the original glycol molecule and does not contain a hydroxyl group.

On the basis of the acetophenone and benzoic acid which separated on oxidation, there may be ascribed to the substance obtained by the dehydration of diphenyl-methyl-phenylacetylenyl-ethylene glycol (VIII), the structure of an unsaturated ketone - methyl-phenyl-phenylacetylenyl-benzoyl-methane (IX).

This ketone can only be formed by a shift of phenyl from the first carbon atom of the pinacol (VIII) to the second and by the separation of water.

Thus, the action of 40% sulfuric acid on methyl-diphenyl-phenylacetylenyl-ethylene glycol caused a pinacolone rearrangement.

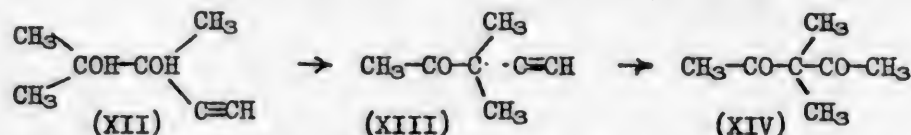
As are shown by the oxidation products, the two other possible products of the pinacolone rearrangement, ketones (X) and (XI), have not been found.



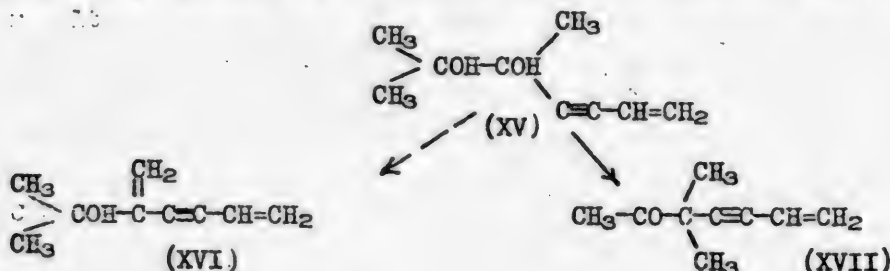
The results obtained show that for the pinacols we examined, independently of the nature of the radicals  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  [Formula (I)], the greater mobility is possessed by the hydroxyl group found in the  $\alpha$ -position to the acetylene bond, i.e. at the second carbon atom.

The increase in the mobility of the hydroxyl found in the  $\alpha$ -position to the triple bond is also seen in pinacols with acetylene and vinyl acetylene radicals and with fatty radicals.

Thus, trimethyl-acetylenyl-ethylene glycol (XII), obtained by A.E. Favorsky and A. S. Onishchenko [6] yields dimethylacetylacetone (XIV) as a result of the pinacolone rearrangement and the succeeding hydration of the acetylenyl ketone (XIII):



The dehydration of trimethyl-vinylacetylenyl-ethylene glycol (XV), studied by I. N. Nazarov [7], in the presence of potassium acid sulfate in vacuo, results in a vinylacetylenyl ketone (XVII) besides the diene carbinol (XVI):



The results we obtained also permit the conclusions that the nature of the transformation of pinacol depends on its structure, and on the nature and relative distribution of the radicals.

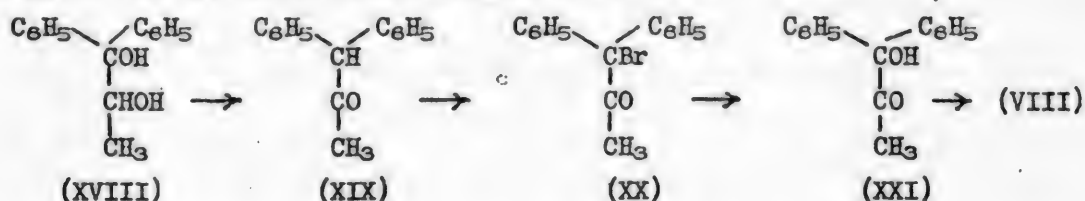
In one of the pinacols the action of sulfuric acid results in a shift of the hydroxyl to the  $\beta$ -position - an acetylene-allene rearrangement, which leads to the formation of an unsaturated  $\gamma$ -ketoalcohol, and then a hydroxydihydrofuran; this was observed for the pinacols (II), (IV), and (V).

In the presence of sulfuric acid other pinacols undergo a dehydration with a shifting of one of the radicals - a pinacolone rearrangement - and was observed to take place with methyl-diphenyl-phenylacetylenyl-ethylene glycol (VIII).

## EXPERIMENTAL

### 1. Synthesis of Diphenyl-methyl-phenylacetylenyl-ethylene Glycol (VIII)

The glycol was synthesized according to the scheme:



Diphenylmethylethylene glycol (XVIII) was synthesized from magnesium-bromophenyl and the ethyl ester of lactic acid with an average yield of 67% of the theoretical, m.p. 95-96° [8].

Unsym. diphenylacetone (XIX) was synthesized by the dehydration of the glycol with sulfuric acid by the method of Tiffeneau [9] and was obtained in two forms - low-melting (m.p. 46°) and high-melting (m.p. 61°). The yield was 86% of theoretical.

Diphenylacetyl bromomethane (XX) has been described by T.I. Temnikova [10] and was synthesized by us by the action of bromine in carbon bisulfide on the ketone under conditions described in numerous works of S.N. Danilov and E.D. Venus-Danilova on the bromination of  $\alpha$ -hydroxyaldehydes [11]. The yield of the bromoketone was 57% of the theoretical, m.p. 55-56°.

In one of the experiments on the bromination of the high-melting form of the diphenylacetone a bromoketone was discovered with a m.p. of 66°. This substance gave a lower melting point in admixture with the bromoketone m.p. 55-56° and upon hydrolysis in the presence of freshly-precipitated barium carbonate it was converted not to diphenylacetylcarbinol (XXI), but to a dark, resinous mass, from which the individual product could not be separated. This high-melting bromoketone was also obtained in small quantities in other bromination experiments. It was separated from the mother-liquors obtained by the recrystallization from hot ligroin of the low-melting bromoketone. According to a private communication of T.I. Temnikova, he also obtained this same high-melting bromoketone in several instances by the bromination of the high-boiling form of diphenylacetone. It was also formed by T.I. Temnikova by the action of phosphorus pentachloride on the ketone.

We did not investigate the bromoketone with a m.p. of 66°, since T.I. Temnikova is concerned with a detailed study of the structure of the bromination

products of diphenylacetone. The normal bromination product of diphenylacetone was of interest to us as the starting material for the synthesis of the keto-alcohol.

Diphenylacetylcarbinol (XXI) was also described by T.I. Temnikova [12] and was obtained by us according to his directions with a yield of 57%; m.p. 65-66°.

Diphenyl-methyl-phenylacetylenyl-ethylene glycol (VIII) was synthesized under the same conditions as those of the pinacols we described earlier. The ether solution of the hydroxy-ketone was added dropwise to the magnesium-bromophenylacetylene obtained. The reaction took place at room temperature, the decomposition by water occurred without heating. After distilling the ether from the ether extract, a thick, dark liquid remained, from which crystals quickly began to separate. Purification on a porous plate and recrystallization from a mixture of petroleum ether and sulfuric ether yielded a finely-crystalline substance, m.p. 119-120°.

As a result of four syntheses (15.6 g magnesium, 73 g bromobenzene, 69 g phenylacetylene and 59.5 g hydroxyketone) 39 g of the pure pinacol was obtained. The yield of the pure product averaged about 51% of the theoretical, based on the hydroxyketone taken:

Analysis of the substance with a m.p. of 119-120°:

0.1190 g substance: 0.3651 g CO<sub>2</sub>; 0.0687 g H<sub>2</sub>O.

0.1259 g substance: 0.3874 g CO<sub>2</sub>; 0.0700 g H<sub>2</sub>O.

Found %: C 83.67, 83.91; H 6.41, 6.17.

C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>: Calculated %: C 84.15; H 6.10.

Determination of the molecular weight:

0.2750 g substance: 29.97 g benzene: Δt 0.145°.

Found: M 316.

C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>. Calculated: M 328.

Cleavage of the pinacol by potassium carbonate [13] confirmed its structure.

## II. Action of Sulfuric Acid of Different Concentration on

### Diphenyl-methyl-phenylacetylenyl-ethylene Glycol.

Experiment I: Action of 30% sulfuric acid: 10 g of the pinacol and 100 ml of 30% sulfuric acid (by weight) were heated to boiling with agitation for 3.5 hours. A dark-brown, viscous liquid was obtained which crystallized. After three recrystallizations from a mixture of ether and petroleum ether, 4.5 g of a substance was separated with a m.p. of 119-120°, not depressing the melting point in admixture with the original glycol. Consequently, pinacol did not change and only partially resinified.

Experiment II. Action of 36% sulfuric acid: Heating the pinacol with 36% sulfuric acid led, after purification and washing with ligroin, to the formation of a crystalline substance with a m.p. of 102-106°, which gave a reaction for the hydroxy group and proved to be a mixture of the original glycol with products of its transformation.

Experiment III. Action of 38% sulfuric acid: Heating 7.8 g of the pinacol with 38% sulfuric acid also gave a mixture of the glycol with its transformation product, m.p. 102-103°, and containing a small quantity of the glycol. Admixture of the product obtained with the original glycol lowered the melting point. On washing the product obtained with ligroin, 0.6 g of a substance was able to be separated with a m.p. of 100-101°, not giving a reaction for the hydroxyl group.



The original pinacol was obtained from the ligroin solution, with a m.p. of 119-120°.

Experiment IV. Action of concentrated sulfuric acid: To 5 ml of sulfuric acid (sp. gr. 1.8), cooled to -6° to -7°, was sprinkled 1.5 g of the glycol in small quantities. At first the mixture turned to an orange color, then to a greenish-brown color. It was allowed to stand in the cooling mixture for 10 minutes, then the temperature was raised to 10°, and the whole mixture poured onto ice. After removing the ether from the ether extract, a dark, resinous substance was obtained which did not crystallize.

Experiment V. Action of 40% sulfuric acid: 6 g of the mixture of the ketone and the products of its transformation, obtained as a result of the previous experiments, was heated with 60 ml of 40% sulfuric acid for 2.5 hours. On cooling the mixture, a dark, resinous, rather viscous layer floated up. The acidic liquid was shown to be very weakly fluorescent; on neutralizing this solution its fluorescence dropped; however, only slight traces of a substance could be separated.

The dark, resinous substance, separated from the acid ether solution, crystallized after the ether was distilled off. The substance is very easily purified by washing on the filter with a porous membrane containing ligroin. 2.2 g of a finely-crystalline substance is then obtained (m.p. 100-101°), not giving a reaction for the hydroxy group; admixture with the original glycol does not lower the melting point. From the ligroin solution, 0.5 g of a substance was separated with a m.p. of 118-120°, corresponding to the original glycol. For the final purification, the substance with a m.p. of 100-101° was recrystallized from alcohol; its melting point does not change in this operation.

Analysis of the substance with a m.p. of 100-101°.

0.1006 g substance: 0.3280 g CO<sub>2</sub>; 0.0539 g H<sub>2</sub>O.

0.1018 g substance: 0.3318 g CO<sub>2</sub>; 0.0554 g H<sub>2</sub>O.

Found %: C 88.92, 88.89. H 5.84, 6.04

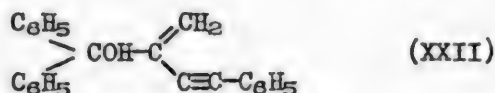
C<sub>23</sub>H<sub>18</sub>O. Calculated %: C 89.03; H 5.80.

0.2207 g substance: 16.28 g C<sub>6</sub>H<sub>6</sub>: Δt 0.23°

Found: M 295.

C<sub>23</sub>H<sub>18</sub>O. Calculated: M 310.

Analysis shows that this substance is obtained as a result of the separation of one molecule of water from the glycol. It may be either a ketone or an enolic alcohol (XXII).



The negative reaction for the hydroxyl group and the results of the investigation compel us to ascribe a ketonic structure to the product obtained by the dehydration of the glycol. However, this proposed ketone does not show a reaction for the carbonyl group; neither a semicarbazone, nor an oxime, nor a hydrazone could be obtained. In all these experiments the substance was recovered without change.

Oxidation of the Ketone C<sub>23</sub>H<sub>18</sub>O with a M.p. of 100-101°

In order to decide which of the three theoretically possible ketones [(IX), (X), or (XI)] corresponds to the substance obtained with a m.p. of 100-101°, it was oxidized with potassium permanganate in a water-pyridine solution.

For the oxidation 2 g of the ketone, 60 ml of freshly-distilled pyridine,

and 3.42 g of potassium permanganate (based on 5 atoms of oxygen to 1 molecule of the ketone) were taken. 2 g of potassium permanganate was dissolved in 75 ml of water and the cold solution gradually added, with vigorous stirring, to the pyridine solution of the ketone; the remaining permanganate (1.42 g) was immediately sprinkled, in a finely-divided state, into the solution until the latter decolorized. The oxidation was continued for 26 hours. The mixture was then heated to 35° for one hour. The color of the potassium permanganate disappeared. The manganese dioxide was filtered by suction, washed with hot water and treated with ether. After distillation off of the ether, 0.2 g of the original ketone was separated. The wash water was combined with the water-pyridine solution and the excess water, pyridine and the volatile, neutral products of oxidation were distilled off with gentle boiling. The residue was extracted with ether to separate any possible neutral products of oxidation not volatile with the water vapor, but none was found to be present. The remaining solution of the salts of organic acids was then evaporated on a water bath for analysis of the oxidation products.

The distilled water-pyridine solution, containing the volatile neutral oxidation products, was neutralized with a quantity of sulfuric acid calculated to combine with the pyridine, and thereafter an ether extraction was made. After the ether was distilled off, 0.6 g of a substance remained which had an odor of acetophenone. The semicarbazone obtained from this product melted at 200-201° and did not lower the melting point upon admixture with the known semicarbazone of acetophenone. From the salts of the organic acids, after decomposition of the dilute sulfuric acid, 1.4 g of an acid was obtained with a m.p. of 116-118° which melted at 121-122° after purification by sublimation, and did not lower the melting point upon admixture with known benzoic acid. After separating the benzoic acid, the acidic liquid was converted to the silver salt, which was separated into three fractions by crystallization. Small quantities of salts were obtained which were stable, not darkening upon standing or evaporation.

#### Analysis of the silver salts:

Fraction I: 0.1475 g of the salt: 0.0696 g Ag.  
 0.1447 g of the salt: 0.0685 g Ag.  
 Found %: Ag 47.18, 47.33.  
 Fraction III: 0.1203 g of the salt: 0.0564 g Ag.  
 Found %: Ag 46.88.  
 $C_7H_5O_2Ag$ . Calculated %: Ag 47.17.

Analysis confirms the fact that only benzoic acid was in the solution.

The analysis of the oxidation products and the formation of two molecules of benzoic acid for each molecule of the ketone (0.7 g of acetophenone and 1.4 g of benzoic acid) indicate that a methyl-phenyl-phenylacetylenyl-acetophenone (IX) structure must be assigned to the ketone obtained.

#### SUMMARY

1. Unsym. diphenyl-methyl-phenylacetylenyl-ethylene glycol was synthesized.
2. Its transformation was studied in the presence of sulfuric acid of various concentrations.
3. The product of the dehydration of this glycol in the presence of 40% sulfuric acid was separated. It was established that this product is a ketone - methyl-phenyl-phenylacetylenyl-acetophenone.
4. It was shown that for unsym. diphenyl-methyl-phenylacetylenyl-ethylene glycol, the principal type of transformation is the pinacolone rearrangement as

distinguished from our previously-investigated pinacols, which, under analogous conditions, isomerize according to the acetylene-allene type of rearrangement.

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• See CB translation p. 159 ff.

## SYNTHESIS OF COMPOUNDS WITH POSSIBLE ANTIMALARIAL ACTION

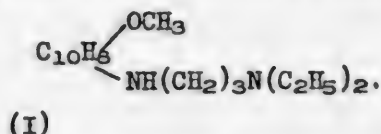
### IV. 4-( $\gamma$ -DIETHYLAMINOPROPYL)-AMINO-1-METHOXY-NAPHTHALENE

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The present work arose in connection with the supposition expressed by V.A. Izmailskii in 1930 on the possibility of the presence of antimalarial action in those aromatic compounds in which the tertiary nitrogen atom of the quinoline nucleus is substituted by a nitrogen atom in a similar electronic condition but not situated in the ring [1,3]. We have such a situation, for example, in the nitrogen atom of the azogroup or the imidol group -  $N = C(OH) -$  (tautomeric -  $NHCO -$  group), contributing, like the nitrogen atom of the quinoline ring, to the resonance of the molecule. A. M. Simonov has undertaken work on the synthesis of compounds of the benzene [1] and benzimidazol [2] series.

We have undertaken the work on the synthesis of compounds of the naphthalene series. We first planned to synthesize a compound of the type (I), containing in the nucleus only



a methoxy-group and a small diamine chain. This arose from the supposition that because of the great similarity between the structures of naphthalene and quinoline, it was possible that the action of this compound would be similar to the action of the plasmocide. We further planned to place a tertiary azo nitrogen atom into compound (I) by introducing a third substituent into the nucleus; this being done by the addition of various diazonium salts of azocompounds.

Among the huge quantities of compounds synthesized in recent years for the purpose of finding new preparations active against malaria, only a very small number of naphthalene derivatives can be found.

E. Fourneau nee Trefouel [4] synthesized 3-dimethylamino-1-( $\alpha$ -naphthyl)-aminopropanol-2 and the corresponding derivative of  $\beta$ -naphthylamine, which were shown to be inactive. Also, E. Fourneau et al. [5] synthesized other amino-alcohols - derivatives of naphthalene: various 3-dialkylamino-1-( $\alpha$ -naphthyl)-propanols- $\epsilon$ , 3-(N-piperidyl)-1-(4'-methoxy- $\alpha$ -naphthyl) propanol- $\epsilon$  and various 3-dialkylamino-1- $\alpha$ (and  $\beta$ )-phenoxypropanols-2. Only for one of these compounds was there established a slight action against the malaria of fowls; however, experiments on humans did not give positive results. In German patent 499826 [6], among a series of compounds, active, in the words of the patent, against the amoeba, there was described 1(- $\beta$ -diethylaminoethyl)-amino-2,3-dimethoxy-naphthalene. King and Work [7] obtained various dialkylaminomethyl- $\alpha$ -naphthyl carbinols, which proved to be inactive against the malaria of fowls inoculated with Plasmodium relictum.

In 1946 a series of works by Jacobs et al. [8] was published, devoted to the synthesis of dialkylaminoalkyl- $\alpha$ -naphthyl-carbinols. Several of these

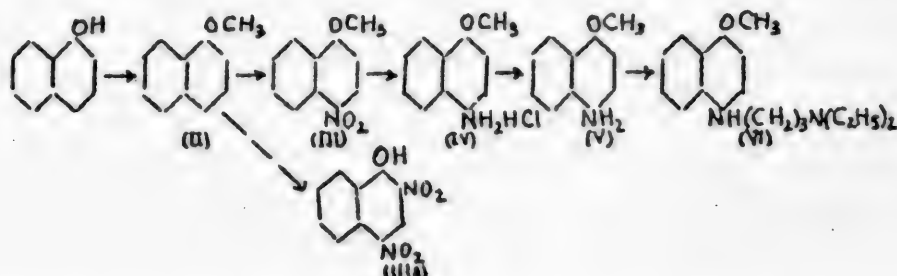


compounds contain the substituents Cl, Br, F,  $\text{OCH}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{O}-$  in the naphthalene nucleus in positions 2, 4, 6, or 7. According to the authors, the dialkylaminomethyl-[2-(or -4-)chloro- $\alpha$ -naphthyl]-carbinol series possesses considerable activity against the inducers of malaria.

Holcomb et al. [9] obtained 2-diethylaminomethyl-1-naphthol, which possesses 10% of the activity of quinine against chicks inoculated with Plasmodium gallinaceum.

Finally, A.M. Simonov [3] recently described the preparation of the N-aminoalkyl derivatives of aminoazo compounds containing the naphthalene nucleus.

In the present paper the synthesis of 4-( $\gamma$ -diethylaminopropyl)-amino-1-methoxy-naphthalene (VI) from  $\alpha$ -naphthol is described, according to the following scheme:



The compound has not been described in the literature. In the nitration of the methyl ether of  $\alpha$ -naphthol (II) with dilute nitric acid a side reaction occurs, as we have previously established; i.e. a desalkylation followed by a nitration of the  $\alpha$ -naphthol formed, to produce 2,4-dinitro- $\alpha$ -naphthol (IIIa). 4-Amino-1-methoxy-naphthalene (V), described in the literature as a dark-colored oil not capable of purification, was obtained by us in the pure state.

In testing our preparation on fowl inoculated with Plasmodium relictum at the Central Tropical Institute of the Ministry of Health of the USSR, under the directorship of Prof. Sh. D. Moshkovsky, no activity was discovered.

On combining 4-( $\gamma$ -diethylaminopropyl)-amino-1-methoxy-naphthalene with phenyldiazonium chloride in an aqueous, water-alcohol or acetic acid solution, a partial decomposition of the diazonium salt was observed with the evolution of nitrogen. Then, upon the addition of  $\text{CH}_3\text{COONa}$  or  $\text{NaOH}$  a red oil separated which could not be purified. The same result was obtained upon combination with p-methoxy-phenyldiazonium chloride.

## EXPERIMENTAL

### Methyl Ether of $\alpha$ -Naphthol (II)

Obtained by us by a method analogous to that proposed by V.A. Izmailskii and Danchev [10] for the preparation of the methyl ether of  $\beta$ -naphthol - by boiling a mixture of  $\alpha$ -naphthol (234 g), methyl alcohol (490 g), and molten zinc chloride (60 g) for 15 hours under a reflux condenser, while passing hydrogen chloride into the reaction mixture. The excess alcohol was then distilled over a water bath. The oil remaining in the flask was separated from the aqueous solution of zinc chloride, washed with water, dried with calcium chloride, and, to separate the unreacted  $\alpha$ -naphthol, redistilled in vacuo until crystals of  $\alpha$ -naphthol appeared in the condenser. For further purification from traces of  $\alpha$ -naphthol the distillate was

shaken several times with a 2% solution of sodium hydroxide; and then several times with a 1% solution of sodium hydroxide to which was added diazosulfanilic acid [11]. After washing with water to remove the azo-dye formed; the product was dried with calcium chloride and subjected to a second vacuum-distillation. 191 g (75% of the theoretical quantity) of an oil liquid was obtained with a pale-green color, which did not change on prolonged standing. B.p. 134-135° (9.5 mm); according to the literature data 101-102° (3 mm), [12]

#### 4-Nitro-1-methoxy-naphthalene (III)

Obtained by us according to the method of Henriques [13] by the addition of 30 g of the methyl ether of  $\alpha$ -naphthol to 50 g of 38% nitric acid (1.56 mol. per mol. of the ether) previously heated to 60°; this being done in a period of 30 minutes with mechanical agitation. After the half-hour agitation at 60° the reaction mixture was poured onto ice. The precipitate was filtered off and washed with water. After two crystallizations from alcohol, carbon having been added, yellow needles were obtained with a m.p. of 83-83.5° (according to the literature data: 83° [13], 85° [14]). The yield was about 40-42% of the theoretical. The yield is not changed by varying the order of mixing of the reagents, by adding the nitric acid to the methyl ether, heated to 60°. By increasing the quantity of nitric acid to 1.3 mol for each mol of the ether, increasing the duration of the reaction to 1 hour, and increasing the temperature to 70°, the yield was increased to 45-47%, and together with the product separated by treatment of the mother liquors after the crystallizations, 53-54% of a substance with the above melting points is obtained.

On heating the crude nitration product (12 g) with 100 ml of a 1% ammonium hydroxide solution, with agitation, until molten, the aqueous solution developed a reddish-brown color. After cooling and filtering off the precipitate, the filtrate was acidified with hydrochloric acid. The light-brown, flocculent precipitate which separated (1.8 g) was recrystallized from chloroform and then from alcohol. Yellow needles, m.p. 139-139.5°. Admixture with 2,4-dinitro- $\alpha$ -naphthol (m.p. 139-139.5°) does not depress the melting point. Thus, we separated 2,4-dinitro- $\alpha$ -naphthol (IIIa) with a yield of about 15% of the theoretical as a side product by the nitration of the methyl ether of  $\alpha$ -naphthol.

#### 4-Amino-1-methoxy-naphthalene Hydrochloride (IV)

In a triple-necked flask, fitted with a stirrer and connected to a reflux condenser, 25 g of 4-nitro-1-methoxy-naphthalene was dissolved in 125 ml of alcohol, by heating on a water bath to 70°. 77 ml of 35% hydrochloric acid was added quickly and 27 g of zinc dust introduced in a period of 5-7 minutes. Another 85 ml of 35% hydrochloric acid was then added and another 28 g of zinc dust was introduced, this addition also lasting 5-7 minutes. The contents of the flask was then heated at 95° for 5 minutes. The color of the solution turned pale brown, becoming colorless after passing through filter paper. Another 10 g of zinc dust was added and after 10 minutes the solution was separated from the zinc precipitate by filtration. The filtrate was transferred to an Erlenmeyer flask, the flask filled with carbon dioxide gas, 215 ml of 35% hydrochloric acid was added and cooled with ice. The precipitate which separated was filtered off, washed with 10% hydrochloric acid and dried in a vacuum desiccator over caustic potash. 21.5-22.5 g of the hydrochloride was obtained as light-gray needles (83-87% of the theoretical quantity). For the purification 20 g of the hydrochloride was dissolved by boiling in 500 ml of water, to which was added 2.5 ml of 35% hydrochloric acid and 2.5 g of sodium chloride (to coagulate the stannous sulfide). After the addition of 1 g of stannous chloride the solution quickly decolorized. A stream of hydrogen sulfide was passed through and the precipitate of stannous sulfide was

\* All melting and boiling points corrected

filtered off. The filtrate was quickly transferred to an Erlenmeyer flask, which was then filled with carbon dioxide and cooled with ice. 170 ml of 35% hydrochloric acid was added and the precipitate which formed was filtered off. The above-described purification was repeated. The yield of the purified product is 80-85% of that taken. Large, colorless or faintly gray needles, not darkening on prolonged standing. M.p. 273-274° (with decomposition); according to the literature data: 278-279° with decomposition [15].

0.2479 g substance: 11.6 ml 0.1 N AgNO<sub>3</sub> (Volhard).

0.2726 g substance: 12.85 ml 0.1 N AgNO<sub>3</sub>.

Found %: Cl 16.51, 16.75.

C<sub>11</sub>H<sub>11</sub>ON·HCl. Calculated %: Cl 16.92.

#### 4-Acetamino-1-methoxy-naphthalene

Obtained by N.N. Vorozhtsov [16] and later by Fierz-David et al. [17] as a dark oil, which they could not purify. After having obtained this substance, these authors, as well as other investigators [13,14], were therefore limited, in their identification, to the preparation and analysis of only the acetyl derivative.

We obtained the substance in the pure state by the following method. 13 g of 4-amino-1-methoxy-naphthalene hydrochloride was mixed with 30 ml of water, then the flask was filled with carbon dioxide gas. 9.5 g of crystalline sodium carbonate was added and heated over a water bath. A dark oil separated. After cooling, a solution of 5 g of potash in 10 ml of water was added. After extraction with ether, the ether extract was dried with potash, and after distilling off the ether the residue was distilled in vacuo under a current of carbon dioxide, the entire product being distilled over in a 1 degree interval. B.p. 152-153° at 1.5 mm. By carefully and rapidly completing all the operations, the distillate - a faint-yellow oil - completely crystallized as a pale-rose mass. M.p. 38.5-39.5°. Weight 8 - 9 g (75-85%). Large, pale-rose needles were obtained by crystallization from 50% alcohol by evaporation. M.p. 39.5-40.5°. In the liquid state the substance quickly darkens in air, in the solid state the darkening takes place slowly.

Analysis of the substance with a m.p. of 38.5-39.5°.

0.2020 g substance: 14.1 ml N<sub>2</sub> (20°, 736.5 mm).

0.1851 g substance: 13.25 ml N<sub>2</sub> (20°, 729.5 mm).

Found %: N 7.87, 8.00.

C<sub>11</sub>H<sub>11</sub>ON. Calculated %: N 8.09.

#### 4-Acetamino-1-methoxy-naphthalene

Obtained by heating a benzene solution of 4-amino-methoxy-naphthalene (m.p. 38.5-39.5°) with acetic anhydride. Yield 90%. M.p. 185.5-186.0°. After recrystallization from 50% alcohol - colorless needles with a m.p. 186.0-186.5°; according to the literature data: 187° [13,14].

#### 4-(γ-Diethylaminopropyl)-amino-1-methoxy-naphthalene (VI)

9.3 g of 4-amino-1-methoxy-naphthalene, 8.8 g of γ-diethylaminopropylchloride (b.p. 73° at 28 mm; 10% excess) and 10 ml of absolute alcohol were placed in a flask connected with a reflux air condenser and fitted with a tube for the admission of carbon dioxide. The mixture was heated on an oil bath for 15 hours: 2 hours at 110°, 1 hour at 120°, and 12 hours at 125-130°, while passing a gentle stream of carbon dioxide over it. After cooling, the contents of the flask crystallized into a homogeneous light-yellow mass, which was dissolved in 60 ml of water.

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Reduced pressure at all times.

After the addition of 14 ml of 37% hydrochloric acid, the solution was filtered from the small quantity of violet precipitate formed. The filtrate was neutralized with a 20% solution of sodium hydroxide, then a solution of 10 g of potash in 10 ml of water was added. The oil which separated was extracted with ether, the ether extract was dried with potash and after distilling off the ether, the residue was distilled in vacuo (2 mm) in a current of hydrogen. At first a small quantity of aminomethoxynaphthalene was distilled (at 160-180°), and then the principal product at 201-202°. Yield was 65-75% of the theoretical quantity; a pale-yellow, thick, oily liquid, gradually darkening in air. The substance is almost insoluble in water, very soluble in alcohol, ether, and benzene.

0.1881 g substance: 16.5 ml N<sub>2</sub> (19°, 729 mm)

0.1551 g substance; 13.4 ml N<sub>2</sub> (19.5°, 729 mm).

Found %: N 9.84, 9.68.

C<sub>18</sub>H<sub>26</sub>ON<sub>2</sub>. Calculated %: N 9.79.

The picrate of 4-(γ-diethylaminopropyl)-amino-1-methoxy-naphthalene was obtained by mixing hot alcoholic solutions of the base with picric acid (1.1 mol. for 1 mol. of the base), as a dark, resinous mass, which changed to crystals of a brownish-orange color after several hours. After crystallization from alcohol, prisms of a brownish-orange color were formed with a m.p. of 125.8-126.5°.

4-(γ-Diethylaminopropyl)-amino-1-methoxynaphthalene Dihydrochloride. By passing hydrogen chloride into a solution of the base in absolute ether, colorless crystals were separated, which were very hygroscopic and quickly deliquesced in air. While being dried to constant weight in vacuo over phosphoric anhydride at 100° and 0.5 mm (5 - 7 hours), the crystals liquefied and changed to a transparent, pale-brown, glassy mass, very easily soluble in water and alcohol. Upon standing, a reddish-violet precipitate gradually separated from the aqueous solution.

The aqueous solution of the dihydrochloride possessed a rather strong local anesthetic action.

0.2134 g of the substance dried at 100°: 11.2 ml 0.1 N AgNO<sub>3</sub> (Volhard)

Found %: Cl 18.66.

C<sub>18</sub>H<sub>26</sub>ON<sub>2</sub>·HCl. Calculated %: Cl 10.99.

C<sub>18</sub>H<sub>26</sub>ON<sub>2</sub>·2HCl. Calculated %: Cl 19.75.

#### SUMMARY

1. The synthesis of 4-(γ-diethylaminopropyl)-amino-1-methoxy-naphthalene from α-naphthol was described. No action was found in tests upon Plasmodium relictum.

2. In the preparation of 4-nitro-1-methoxy-naphthalene by the nitration of the methyl ether of α-naphthol with 38% hydrochloric acid, it was found that 2,4-dinitro-α-naphthol is formed as a side-product in a quantity of about 15% of the theoretical.

3. 4-Amino-1-methoxy-naphthalene was obtained in the pure state, and its properties described.

This work was subsidized by the Central Tropical Institute of the Ministry of Health of the USSR, to the direction of which we express our thanks. The author wishes to express his sincere appreciation to Prof. V. A. Izmailskii for his interest in the work, and to Prof. Sh. D. Moshkovskii for testing the preparation.



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## REACTION OF ANABASINE WITH MINERAL ACIDS

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The alkaloid anabesine, separated by A.P. Orekhov, possesses definite basic properties. And because of the fact that its molecule contains piperidine and pyridine rings, it may be postulated that anabesine will form crystalline salts with strong mineral acids. Since these salts are unknown in the literature, we undertook the problem of investigating the conditions for their preparation.

Preparation of Anabesine Hydrochloride. For our work we used anabesine with a b.p. of 138-140° at 12 mm pressure, separated from crude anabesine with according to the method recommended by A. S. Sadykov and G. V. Lazuryevski [2].

For preparing anabesine hydrochloride, the anabesine must first be dissolved in some solvent, and then hydrogen chloride passed through this solution; the reaction proceeds smoothly. If the solvent taken is benzene, then the formation of crystalline anabesine hydrochloride takes place rather easily. It is especially convenient to obtain anabesine hydrochloride if the solvent taken is acetone. Anabesine hydrochloride is separated as a white crystalline precipitate, when a gentle stream of hydrogen chloride is passed through the solution of anabesine in acetone, the solution being cold and carefully agitated.

The anabesine so obtained we filtered off on a Buchner funnel. After repeated washings with acetone and drying in a vacuum-desiccator, m.p. 194°. The yield of the dry salt is about 80%. The anabesine hydrochloride obtained is stable and quite hygroscopic.

Anabesine hydrochloride is easily soluble in water, alcohol, chloroform and with heating in dichloroethane. We could not recrystallize the hydrochloride, since it is extremely soluble in water and alcohol, and from solutions in dichloroethane, light-brown crystals with a lower melting point separated. The salt obtained from the solution of anabesine in acetone was therefore subjected to analysis.

0.1228 g substance: 0.2752 g CO<sub>2</sub>; 0.0874 g H<sub>2</sub>O.

Found %: C 61.10; H 7.96; Cl 17.72.

C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>·HCl. Calculated %: C 60.45; H 7.61; Cl 17.74.

Preparation of the Nitric Acid Salt of Anabesine. As in the preparation of the hydrochloride, we obtained anabesine nitrate by the addition of nitric acid to solutions of anabesine in various solvents.

Anabesine nitrate is easily separated in the crystalline form only from solutions of anabesine in acetone. To accomplish this, fuming nitric acid is gradually added dropwise and with continuous stirring to the solution of anabesine in acetone. Since a large amount of heat is evolved in the reaction the solution must be strongly chilled. The nitrate salt which separates is a white, finely-crystalline powder, soluble in excess acid. The acetone remaining after washing

and filtering off the anabesine nitrate was removed in a vacuum-desiccator. The yield of the dry salt is about 70%.

Anabesine nitrate is stable in air, melts at  $163^{\circ}$ , and is easily soluble in water and alcohol. From the alcoholic solution of anabesine nitrate, after long standing, we were able to obtain a small quantity of colorless crystals with a m.p. of  $167.5^{\circ}$ . The salt obtained from the solution of anabesine in acetone was subjected to analysis.

0.1040 g substance: 0.2042 g  $\text{CO}_2$ ; 0.0648 g  $\text{H}_2\text{O}$ .

Found %: C 53.55; H 6.97;  $\text{NO}_3$  27.30.

$\text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HNO}_3$ . Calculated %: C 53.32; H 6.71;  $\text{NO}_3$  27.54.

If sulfuric acid is carefully added to a solution of anabesine in acetone, with continuous shaking anabesine sulfate separates as white crystalline flakes, soluble in excess acid; however, on filtration this salt becomes viscous and it is impossible to remove it from the funnel. This attests to the great hygroscopicity of the compound obtained; we therefore could not separate and analyze the sulfate.

#### SUMMARY

1. A crystalline compound of anabesine with hydrogen chloride was obtained of the composition  $\text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HCl}$ .
2. A crystalline compound of anabesine with nitric acid was obtained of the composition  $\text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HNO}_3$ .

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# STRUCTURE OF HETEROPOLY ACIDS FROM DATA ON THE INVESTIGATION OF POTASSIUM SILICOTUNGSTATES

E. A. Nikitina and A. S. Kokurina

Silicotungstic acids and their salts belong to a number of practically important and theoretically interesting heteropoly compounds. They have been as yet very incompletely investigated and besides, an investigation of these compounds should bring a certain amount of additional clarity to the general theory of the structure of heteropoly acids. We started the experiments with potassium cis-silicotungstic acids. Since the basis of all our work was a certain aspect of the structure of heteropoly acids, we will briefly present the later works in this field, i.e., after 1939. Work up to 1939 has been examined by E.A. Nikitina in a separate paper [1].

The investigations of Kraus, performed from 1938 to 1939, resulted in his upholding the opinions of Keggin on the structure of heteropoly acids, i.e., he considers silicotungstic (which we will call hereafter s.t.) acid to be quadribasic, and acids with a central atom - phosphorus - to be tribasic, etc.[2].

At the end of 1939 Kraus [3] synthesized an octa-substituted iron silicotungstic acid and arrived at the conclusion that s.t. acid is octa-basic, i.e., confirmed the conception of Miolati-Rosenheim on the basicity of heteropoly acids. In 1940 Jander [4], comparing the available material in the literature on the synthesis of highly-substituted salts of heteropoly acids with data from structural analysis, according to Keggin, expressed the opinion that the works of Keggin do not disprove the position taken on the high basicity of heteropoly acids, since in the molecules of water (HOH), which are always present in heteropoly acids, either H, under the influence of the large number of  $(W_3O_{10})_4$  radicals, may acquire the properties of acid  $H^+$  and become substituted by a metal. Pierre Souchay [5], in a series of later works (1943-1946), refutes the theory of Miolati-Rosenheim, postulating that s.t. acid is quadribasic, and adheres to the opinions of Keggin on the structure of heteropoly acids. In 1946, Marcel Jean [6] obtained a quadri-substituted copper silicotungstate and on the basis of this confirms the concept that s.t. acid is quadri-basic, in accordance with the views of Keggin. Such are the results of the more recent research on the question of the structure of heteropoly acids. In the present communication we will present results of an investigation, which give very substantial proof of the Miolati-Rosenheim theory of the structure of heteropoly acids.

Cis-silicotungstic Acid. The classical work of Marignac [7] describes methods for obtaining cis-s.t. acid: the first method consists of the action of excess sulfuric acid on potassium s.t. acid; according to the second method mercury s.t. is decomposed by hydrochloric acid and hydrogen sulfide. The first method was discarded by Marignac himself, since it did not result in the synthesis of a pure preparation, and always led to the formation of acids with a considerable content of potassium salt. Under our conditions, the second method was not quite convenient; we therefore utilized the later investigations of Rosenheim [8], Copaux [9], Wu [10], North and Beal [11] and others, employing the reaction for the formation of sodium s.t. from sodium tungstate and silicate in an acid medium, with the subsequent formation of the etherate of cis-s.t. acid followed by its decomposition to form the desired compound.



Our experiments showed that the reaction forming the  $[\text{Si}(\text{W}_2\text{O}_7)_6]$  ion takes place only under certain conditions. We obtained the most favorable results when we used a 30% solution of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , sodium silicate solution sp. gr. 1.38 at 15° and hydrochloric acid sp. gr. 1.17-1.18. For each experiment the following quantities had to be used:  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  - 800 g,  $\text{Na}_2\text{SiO}_3$  - 29 g, and hydrochloric acid sp. gr. 1.18 - 500 ml.

To the mixed solutions of sodium tungstate and silicate, heated to boiling, was added a calculated quantity of hydrochloric acid, dropwise from a separatory funnel. The first portion of the hydrochloric acid resulted in the formation of a precipitate of  $\text{H}_2\text{WO}_4$ , which dissolved on further heating. After the addition of 1/3 of the quantity of hydrochloric acid required, silicic acid began to separate simultaneously with the tungstic acid. After the addition of half the volume of hydrochloric acid, the quantity of silicic and tungstic acids were markedly decreased as a result of complex formation. Towards the end of the reaction, when 1/8 of the required amount of hydrochloric acid remains unadded, the solution becomes clear and precipitation of  $\text{H}_2\text{WO}_4$  by the further addition of hydrochloric acid does not occur, but a small quantity of silicic acid remains as an insoluble precipitate to the very end of the reaction.

TABLE 1

Exp. No.	Found (in %)				Calculated from the formula (in %)			Water of hydration (moles)	Molarity of the solution	pH
	$\text{WO}_3$	$\text{SiO}_2$	$\text{H}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{WO}_3$	$\text{SiO}_2$	$\text{H}_2\text{O}$			
1	90.87	2.02	6.78	—	95.47	2.06	2.46	7.11	0.01	1.3-1.5
2	88.28	1.70	10.34	—	—	—	—	12.91	—	—
3	87.87	1.72	10.10	0.35	—	—	—	12.52	—	—
4	88.29	1.80	10.18	0.18	—	—	—	12.65	—	—

After the addition of all the hydrochloric acid, the solution is filtered hot to remove the precipitate of silicic acid. The cooled filtrate is treated with ether and is further acidified by an additional 300 ml of hydrochloric acid. Upon shaking the solution in a separatory funnel the etherate of s.t. acid deposits on the bottom as oily drops of a yellow color. The etherate is separated and the free cis-s.t. acid is crystallized isothermally from it in air. It is possible to distil off the ether on a water bath and then obtain the crystalline s.t. acid; however, this second method of crystallization yields small, poorly-formed crystals; by the first method beautiful, cubic octahedrals of the cis-s.t. acid are obtained. The yield of the preparation is 70%.

Results of the analyses of several samples of s.t. acid are given in Table 1.

The results obtained (Table 1) indicate that preparation 3 contains an admixture of 0.35%  $\text{Na}_2\text{O}$ ; in preparation 4 the  $\text{Na}_2\text{O}$  content is 0.18%; this decrease in  $\text{Na}_2\text{O}$  content resulted from the fact that the acid was extracted with ether a second time.

#### Potassium Cis-silicotungstate

Marignac described three potassium cis-silicotungstates (which we will hereafter call potassium c.s.t.). By the action of silica gel on a solution of potassium p-tungstate, keeping the solution neutral, Marignac obtained a quadri-substituted salt in the form of hexagonal prisms. By the action of excess sulfuric acid on the quadri-substituted potassium c.s.t., Marignac obtained prismatic crystals of a mono-substituted potassium c.s.t.

Marignac also obtained silico-10-tungstic acid. By the addition of eight equivalents of potash to it, Marignac separated an octa-substituted salt of silico-10-tungstic acid and an octa-substituted potassium silicotungstate by fractional crystallization. By the addition of four equivalents of potash to a solution of silico-10-tungstic acid, Marignac separated, by fractional crystallization, a mixture of quadri-substituted salts of cis- and trans- s.t. acids and then quadri-substituted potassium salts of silico-10-tungstic and silico-11-tungstic acids. Conversion of Marignac's analyses to the anhydrous components indicates that he obtained compounds of the correct composition.

Kehrmann [12] confirmed the analyses of Marignac's salts as well as the free c.s.t. acid. Having determined, however, only the total sum of the oxides  $\text{WO}_3 + \text{SiO}_2$ , and having determined  $\text{SiO}_2$  by a method which gives up to 15-20% error, Kehrmann came to the conclusion that the octa-substituted salt of Marignac corresponds to the composition  $7\text{K}_2\text{O} \cdot 2\text{SiO}_2 \cdot 20\text{WO}_3$ , i.e., an octa-substituted potassium c.s.t., but such a compound does not exist.

Rosenheim obtained a quadri-substituted potassium c.s.t. by saturating a solution of potassium p-tungstate in hydrochloric acid with silicic acid. He also tried to obtain the octa-substituted salt from the quadri-substituted, adding four equivalents of potash all at once, but only obtained a salt of the composition  $\text{K}_7\text{H}[\text{Si}(\text{W}_2\text{O}_7)_5] \cdot 11\text{H}_2\text{O}$ .

Scroggie and Clark [13] studied the neutralization of c.s.t. acid and established that on the addition of 11 equivalents of potassium hydroxide, a slight Scheele reaction took place in the solution. The Scheele reaction became more definite upon the addition of 12 equivalents of KOH. After introducing 14 equivalents of potassium hydroxide, adding the hydrochloric acid and separating the precipitate of tungstic acid, Scroggie and Clark separated a small quantity of the etherate of silico-10-tungstic acid. Experiments conducted analogously, but with the addition of 18 and 20 equivalents of KOH to the solution of s.t. acid, resulted in the isolation by Scroggie and Clark of, according to them, silico-8-tungstic and silico-7-tungstic acids. A weak point of the work is the extreme scantiness of the analytical data.

According to Scroggie and Clark, all the s.t. acids (i.e., 12-, 10- and 8-tungstic) are quadribasic [14].

Pierre Souchay [15] believes the potassium silico-10-tungstate described in the literature by Marignac and others to be a silico-11-tungstate and denies the existence of any other potassium silicotungstates with the exception of salts of the 12th and 11th series of acids.

We began our study of potassium s.t. with the synthesis of a quadri-substituted potassium s.t. After a series of preliminary experiments we established a method for the preparation of potassium c.s.t. of the composition  $\text{K}_4\text{H}_4[\text{Si}(\text{W}_2\text{O}_7)_6] \cdot x\text{H}_2\text{O}$ . The starting materials must be used in the indicated concentrations: 6% solution of potassium p-tungstate, solution of potassium silicate sp. gr. 1.27 at a temperature of about 15°, and hydrochloric acid sp. gr. 1.17-1.18. For each experiment the following quantities were used: 6% solution of potassium p-tungstate - 3 liters, solution of potassium silicate - 150 ml, hydrochloric acid - 90 ml.

The solution of potassium p-tungstate and silicate was heated to boiling, and hydrochloric acid was added to the boiling solution. After the addition of all the hydrochloric acid the solution was boiled, then warmed on a water bath and filtered off from the excess silicic acid. A clear solution was obtained with a sp. gr. of 1.05-1.07 at 15° and containing 5.71-5.73 g of HCl per liter. It was set aside to crystallize. The evaporation was carried out to 1/3 of the

initial volume; on cooling to room temperature, beautifully formed, hexagonal crystals of potassium c.s.t. separated; occasionally, semi-spherical nodules of rare beauty were formed. The salt effloresces somewhat on exposure to air.

TABLE 2

Fraction 1  $K_4H_4[Si(W_2O_7)_6] \cdot xH_2O$ ; acidity 13.66 g HCl in 1 liter.

Exp. No.	Found (in %)					Recalculated to the anhydrous salt (in %)			Calculated according to the formula (in %)			Molarity of the solution	pH
	WO <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	H <sub>2</sub> O	Cl	WO <sub>3</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	WO <sub>3</sub>	K <sub>2</sub> O	SiO <sub>2</sub>		
1	85.76	1.92	6.26	5.44	0.25	91.64	6.34	2.05	91.8	6.25	1.97	0.009	2-3
2	83.66	1.91	6.25	8.22	0.33	91.55	6.35	2.09					
3	83.85	1.66	5.79	8.81	0.02	91.90	6.35	1.82					
4	83.32	1.58	5.83	9.17	0.07	91.92	6.56	1.74					
5	82.23	1.74	5.65	10.26	0.025	91.78	6.30	1.94					

After removing the crystals, the mother liquor, volume about 2 liters, had a sp. gr of 1.12-1.15 and the content of free hydrochloric acid was 13.66-13.70 g in 1 liter. The solution was set aside to crystallize and once more evaporated to 1/3 its initial volume. The crystallization was conducted under the conditions described above. The second fraction of crystals obtained from this solution consisted of a quadri-substituted potassium c.s.t. and a small quantity of potassium chloride. After separating the second fraction of crystals, the mother liquor had a sp. gr. of 1.18, free hydrochloric acid content 24.36 g in 1 liter, and a volume of 1.5 liters.

In Table 2 are given results of the analyses of the samples of quadrisubstituted potassium c.s.t. which we synthesized and which were obtained by separating the first fraction of crystals from the reaction solution. By our method of preparation we always encountered only the cis-isomer. We studied all the separated fractions microscopically.

It is evident from Table 2 that from the composition of the compounds obtained a rather close correspondence to the quadri-substituted salt of c.s.t acid is indicated.

In the second fraction of the synthesis of potassium c.s.t. the salt separated is quite contaminated with potassium chloride.

TABLE 3

Fraction 2  $K_4H_4[Si(W_2O_7)_6] \cdot xH_2O$ ; acidity 24.36 g HCl in 1 liter.

Exp. No.	Found (in %)					Recalculated to the anhydrous salt (%)			Calculated according to the formula (%)		
	WO <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	H <sub>2</sub> O	Cl	WO <sub>3</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	WO <sub>3</sub>	K <sub>2</sub> O	SiO <sub>2</sub>
1	82.36	5.82	1.67	9.96	0.25	92.01	6.27	1.87	91.8	6.25	1.97
2.	79.52	8.86	1.58	8.87	1.07	89.82	8.70	1.78			
3	58.29	19.82	0.88	8.00	13.21	94.73	3.74	1.43			

Results of the analysis of the samples are given in Table 3.

By further evaporation of the mother liquor, the potassium c.s.t obtained from the second fraction is still more contaminated by potassium chloride;

therefore further evaporation would be quite useless. As a rule we concluded the evaporation with the separation of the second fraction of potassium c.s.t. We conducted various experiments, evaporating solutions of potassium c.s.t. to dryness, and we observed that with a decrease in the volume of the solution and increase in its acidity,  $H_2WO_4$  began to separate due to the decomposition, in a strongly acid solution, of small quantities of potassium c.s.t. remaining in the mother liquor.

It must therefore be concluded that the silicotungstic anion is definitely related to the concentrations of acid. In order to confirm our conclusion we conducted one more experiment: four 2 g weights of potassium c.s.t. were taken; each of these was treated with equal volumes of hydrochloric acid of different concentrations, containing 5, 10, 15 and 24.78% HCl. After this treatment all the tests were placed in a thermostat for two hours. We then observed that the salt samples with 5 and 10% hydrochloric acid did not undergo any external change; the potassium c.s.t. which dissolved on the initial heating began partially to crystallize on the walls of the test tube. In the sample with 15% potassium c.s.t., solution was not complete, and the white crystals of the salt gradually began to yellow and after two hours the potassium c.s.t. almost completely decomposed with the formation of  $H_2WO_4$ .

TABLE 4

Analysis of an individual crystal of  $K_3H_5[Si(W_2O_7)_6] \cdot xH_2O$

	Found (in %)	Recalculated to the anhydrous salt (%)	Calculated according to the formula (%)
WO <sub>3</sub> .....	86.01	93.12	93.27
SiO <sub>2</sub> .....	1.84	2.03	2.01
K <sub>2</sub> O .....	4.47	4.84	4.73
H <sub>2</sub> O .....	7.68		

In the test tube with 25% acid a visible solution of the salt did not occur and after 10 minutes of heating the entire sample decomposed with the separation of  $H_2WO_4$ .

In the test tube with a 5% solution of acid an individual crystal with a regular system quickly began to grow. Analysis of the crystal showed that we had obtained a tri-substituted salt of c.s.t. acid, as is evident from Table 4.

Thus, a reaction took place here in which the base was split from the quadri-substituted salt. A similar type of reaction with heteropoly salts was observed by Marignac, Brandgorst and Kraut, A.V. Rakovskii and E.A. Nikitina.

Hexa-substituted Potassium C.s.t. To obtain the hexa-substituted salt an almost saturated solution of quadri-substituted potassium c.s.t. was taken, having the composition K<sub>2</sub>O 6.33%, SiO<sub>2</sub> 1.70%, WO<sub>3</sub> 92.02%. A quantity of potassium hydroxide, calculated according to the equation, was added to it in two increments. The reaction mixture was carefully mixed and allowed to stand in a desiccator, to accomplish an isothermal crystallization at room temperature. After approximately four hours of standing, small cubical crystals of a salt began to separate. Their analysis is shown in Table 5 (No. 1).

We obtained the hexa-substituted potassium c.s.t. in the following series of experiments by lowering the acidity in the condensation reaction of the silicate and p-tungstate. We took those concentrations of the reacting substances used in



the synthesis of the quadri-substituted salt, but the quantity of hydrochloric acid was cut in half.

We obtained small, white cubical crystals having a regular system, the analytical results of which are given in Table 5 (No. 2).

TABLE 5  
Analyses of hexa-substituted salts

Exp. No.	Found (in %)				Recalculated to the anhydrous salt (in %)			Calculated according to the formula (%)			Molarity of the solution	pH
	WO <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	H <sub>2</sub> O	WO <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	WO <sub>3</sub>	K <sub>2</sub> O	SiO <sub>2</sub>		
1	74.35	1.66	8.14	15.90	88.36	1.97	9.67	89.06	9.02	1.92	0.009	5.2-6
2	79.36	1.75	8.93	9.80	88.14	1.94	9.92					

As is shown by the analysis, in both cases there was obtained a hexa-substituted salt with a small admixture of a hepta-substituted.

To obtain salts still richer in potassium, it seemed quite inexpedient to do so by lowering the acidity, since the reaction of mixed potassium p-tungstate and silicate solutions approached the alkaline side and the formation of  $[\text{Si}(\text{W}_2\text{O}_7)_6]^{VIII}$  was hindered. Therefore, to obtain potassium salts rich in potassium, we applied the neutralization method to the more acid salts.

A solution of the hexa-substituted salt was neutralized with potassium hydroxide, using a quantity calculated to obtain the hepta-substituted salt. It was then crystallized isothermally, in a desiccator at room temperature, i.e. about 15°.

The hepta-substituted salt obtained was neutralized by a quantity of potassium hydroxide calculated to obtain the octa-substituted salt. We obtained the hepta-substituted and octa-substituted salts as small, white, cubical crystals. The results of analysis of the compounds are given in Table 6.

We did not limit ourselves to the study only of highly-substituted salts; we also obtained all the lower-substituted salts. Starting from the free acid and neutralizing it by a calculated quantity of potassium hydroxide, we obtained the mono-substituted salt by isothermal crystallization in a desiccator; from the mono-substituted salt the di-substituted salt was obtained, etc.

The analytical results of all the salts obtained are shown in Table 6.

All the compounds of potassium c.s.t. we synthesized are easily freed from admixture of Cl<sup>-</sup> by one or two recrystallizations. All the salts obtained in aqueous solution had an acid reaction to litmus. This situation prompted us to study the pH of solutions of the free acid and all its salts by a colorimetric method; the results are shown in Tables 1, 2, 5 and 6.

The pH of solutions of c.s.t. acid equals 2.54 according to the measurements of Brauer [16]; our pH measurements indicate that free c.s.t. acid is a strong acid; the behavior of its salts in aqueous solution confirms this property.

Since the hepta-substituted salt gives a weakly-acid reaction in aqueous solution, we decided to obtain all the possible members of the potassium s.t. series up to the complete decomposition of the heteropoly anion.

Highly-substituted Potassium Silicotungstates. The first highly-substituted

(nona-substituted) salt was obtained by us by the action of a calculated quantity of potassium hydroxide on an almost saturated solution of the quadri-substituted salt. The KOH, in a 10% solution, was gradually added in increments, each of which corresponded to the addition of one equivalent. The solution was then carefully mixed for 5-10 minutes, the next equivalent of alkali was then added, etc. The solution of potassium s.t. was crystallized isothermally, in a desiccator at a temperature of about 15°.

We used the quadri-substituted potassium c.s.t. as a starting material since the method of its preparation had been well established by us. The addition of the potassium hydroxide solutions in single increments and in the indicated volume enabled us to carry out more quickly the synthesis of all the potassium s.t. In several cases we crystallized one or another highly-substituted salt and added to its solution one equivalent of potassium hydroxide, thus obtaining a salt with a still higher substitution. After crystallization the samples of all the salts were dissolved in water and the formation of their silico-tungstate anion controlled by the Scheele reaction. With the substitution of nine atoms of hydrogen by potassium the solution acquired a weakly-alkaline reaction. However, the Scheele reaction, besides being of small influence, was found only in crystals of the salt obtained by substituting the 21st hydrogen atom:

In Table 7 are given the analytical results of all the higher-substituted salts. We indicate them as K<sub>9</sub>, K<sub>10</sub>, etc., which at the same time points out the number of hydrogen atoms substituted by the metal. In the last column is shown the pH as determined by the colorimetric method.

The highly-substituted salts obtained, from K<sub>9</sub> to K<sub>13</sub>, are evidently solid solutions of octa-substituted potassium c.s.t. and silico-11-tungstates.

Table 6

Test No.	Formulas of the salts	Found (in %)					Recalculated to the anhydrous salt (%)					Calculated according to the formula					Molarity of the solution	pH
		W <sub>02</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	H <sub>2</sub> O	Cl	W <sub>02</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	H <sub>2</sub> O	Cl	W <sub>02</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	H <sub>2</sub> O	Cl		
1	KH <sub>7</sub> [Si(W <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ]·xH <sub>2</sub> O . . .	85.66	1.61	1.86	10.95	none	96.05	1.80	2.05	96.30	1.63	2.07	0.01	1.5-2.0				
2	K <sub>2</sub> H <sub>6</sub> [Si(W <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ]·xH <sub>2</sub> O . . .	87.18	3.09	1.83	3.23	none	94.65	3.33	1.99	94.76	3.28	2.04	0.01	2-3				
3	K <sub>3</sub> H <sub>5</sub> [Si(W <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ]·xH <sub>2</sub> O . . .	86.01	4.47	1.84	7.68	none	93.1	4.84	2.03	93.27	4.73	2.01	0.009	2-3				
4	K <sub>4</sub> H <sub>4</sub> [Si(W <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ]·x <sub>2</sub> H <sub>2</sub> O . . .	85.48	4.68	1.79	8.03	none	92.93	5.04	1.95	93.27	4.73	2.01	0.009	4.6-5.2				
5	K <sub>5</sub> H <sub>3</sub> [Si(W <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ]·xH <sub>2</sub> O . . .	84.13	7.09	1.83	6.68	0.27	90.77	7.64	1.47	90.40	7.68	1.95	0.009	5.2-6				
6	K <sub>6</sub> [Si(W <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ]·xH <sub>2</sub> O . . .	87.44	7.12	1.87	3.43	none	90.61	7.38	1.94	90.40	7.68	1.95	0.009	6.65				
		82.11	9.89	1.79	6.18	none	87.77	10.30	1.91	87.73	10.39	1.85	0.008					
		79.55	10.93	1.82	7.60	none	86.09	11.83	1.97	86.46	11.74	1.86						

TABLE 7

Highly substituted salt	Found (in %)					Recalculated to the anhydrous salt (in %)			pH of a 0.01 N solution
	K <sub>2</sub> O	SiO <sub>2</sub>	WO <sub>3</sub>	Cl	H <sub>2</sub> O	K <sub>2</sub> O	SiO <sub>2</sub>	WO <sub>3</sub>	
K <sub>9</sub> .....	11.51	1.79	79.93	0.01	6.81	12.36	1.92	85.72	7.6 - 8
K <sub>10</sub> .....	11.41	1.79	79.72	0.01	7.08	12.27	1.92	85.79	7.6 - 8
K <sub>11</sub> .....	11.50	1.86	79.86	none	6.77	12.38	1.99	85.67	7.6-- 8
K <sub>12</sub> .....	11.50	1.89	79.88	none	6.73	12.33	2.03	85.64	7.6 - 8
K <sub>13</sub> .....	11.65	1.78	78.82	none	7.73	12.64	1.93	85.44	7.6 - 8
K <sub>14</sub> .....	11.68	1.86	78.70	none	7.78	12.66	2.01	85.32	7.6 - 8
K <sub>15</sub> .....	11.86	2.04	79.33	none	6.86	12.67	2.19	85.15	7.6 - 8
K <sub>16</sub> .....	11.81	3.11	76.44	none	8.70	12.93	3.40	83.67	7.6 - 8
K <sub>17</sub> .....	11.86	2.43	77.99	none	7.71	12.85	2.63	84.51	7.6 - 8
K <sub>18</sub> .....	11.76	3.11	76.29	none	8.82	12.90	3.41	83.69	7.6 - 8
K <sub>19</sub> .....	12.26	2.10	75.16	none	9.46	13.54	3.42	83.03	7.6 - 8
K <sub>20</sub> .....	12.08	3.90	74.84	none	9.19	13.30	4.29	82.40	-
K <sub>21</sub> .....	12.11	4.14	74.50	none	9.24	13.34	4.56	82.10	8 - 8.8
K <sub>22</sub> .....	12.35	6.32	72.86	none	8.51	13.50	6.90	79.60	8 - 8.8
	12.18	6.42	71.87	none	9.52	13.47	7.09	79.44	-

The K<sub>14</sub> salt is an individual octa-substituted salt of silico-11-tungstic acid. The K<sub>15</sub> salt is, according to its properties, similar to the hepta-substituted salt of silico-10-tungstic acid. The K<sub>17</sub> salt corresponds to the hepta-substituted salt of silico-9-tungstic acid. The K<sub>16</sub>, K<sub>18</sub>, and K<sub>19</sub> salts are octa- and nona-substituted salts of silico-6-tungstic acid. The K<sub>20</sub> salt is a quadri-substituted salt of silico-5-tungstic acid. Finally, the K<sub>21</sub> and K<sub>22</sub> salts are double salts of potassium p-tungstate and silicate. The analytical data compared in Table 8 are recalculated to the anhydrous components and the composition of the compounds obtained calculated according to the formula.

TABLE 8

Exp No.	Salt	Found (in %)				Calculated (in %)		
		K <sub>2</sub> O	SiO <sub>2</sub>	WO <sub>3</sub>	H <sub>2</sub> O	K <sub>2</sub> O	SiO <sub>2</sub>	WO <sub>3</sub>
1	Potassium-silico-11-tungstate	12.66	2.01	85.35	-	12.60	2.01	85.38
2	Potassium-silico-10-tungstate	12.67	2.19	85.17	-	12.17	2.21	85.62
3	Potassium-silico-9-tungstate	12.85	2.63	84.51	-	12.32	2.42	84.28
4	Potassium-silico-6-tungstate	12.90	3.41	83.69	-	11.49	3.66	84.85
5	Potassium-silico-5-tungstate	13.30	4.29	82.40	-	13.37	4.26	82.55
6	Double salt 5K <sub>2</sub> O·12WO <sub>3</sub> ·K <sub>2</sub> SiO <sub>3</sub> ·21H <sub>2</sub> O	12.35	6.32	72.86	8.51	21.87	6.20	71.94

In obtaining the K<sub>17</sub>, K<sub>18</sub>, and K<sub>21</sub> salts, second fractions of s.t. salts were fractionated. The compounds obtained did not give the Scheele reaction and were, as is shown by analysis, potassium salts of silico-9-, 10- and 7-tungstic acids. The results of the analysis of these salts are given in Table 9; calculations from the formula are also given therein for comparison.

In the course of this work the K<sub>17</sub>, K<sub>18</sub>, K<sub>19</sub>, K<sub>21</sub>, and K<sub>22</sub> salts were kept in closed test tubes for 3½ months; at the end of this time we had to prepare their aqueous solution anew. We should state here that these compounds were completely soluble up to this time but the newly prepared solutions contained

different quantities of insoluble silicic acid; the precipitate was especially great in the  $K_{22}$  salt. When we tested the pH of the solutions we also noted that the pH shifted closer to the neutral point; the  $K_{21}$  and  $K_{22}$  salts ceased to exhibit the Scheele reaction.

TABLE 9

Analysis of the Second Fractions of Potassium s.t.  
and of the Salts Obtained After Conversion

Highly substituted salt		Found (in %)				Recalculated to the anhydrous salt (%)			Salts belong to:	pH of 0.01 N solution
		H <sub>2</sub> O	K <sub>2</sub> O	SiO <sub>2</sub>	WO <sub>3</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	WO <sub>3</sub>		
Second fractions	K <sub>17</sub>	7.95	12.80	2.30	77.25	13.86	2.49	89.65	9 series	—
	K <sub>18</sub>	8.78	12.96	1.95	76.31	14.21	2.13	83.66	10 series	—
	K <sub>19</sub>	8.63	12.59	2.87	76.00	14.67	3.14	83.19	7 series*	—
After transformation	K <sub>18</sub>	6.76	11.77	1.76	79.71	12.33	1.89	85.49	Solid solution of salts of the 11th and 12th series	7.6-8
	K <sub>22</sub>	7.01	11.96	2.86	78.18	12.86	3.08	84.06		7 series
K <sub>17</sub> K <sub>19</sub> K <sub>21</sub>		—	—	—	—	14.36	3.05	82.59	—	7.6-8

Consequently, a rearrangement took place in these salts, in which the double salts shifted to heteropoly salts. We determined the amount of SiO<sub>2</sub> formed as a result of the transformation in the  $K_{18}$  and  $K_{22}$  salts; in the first salt we found 1.29% SiO<sub>2</sub> and in the second, 3.40% SiO<sub>2</sub>. From the quantity of free silicic acid separated in the free condition we should expect that in the crystallization there should be further obtained from these salts compounds of the 11th or 12th series in the first case, and salts of the 6th or 7th series in the second case. After removing the silicic acid, solutions of the  $K_{18}$  and  $K_{22}$  salts crystallized in the desiccator isothermally. Analysis of the crystals obtained showed a rather close agreement with the calculated, which may be made on the basis of the determination of the precipitated silicic acid.

Evaluation of Results. As is shown by this work, c.s.t acid is octabasic, which is in complete agreement with the theoretical considerations of Miolati-Rosenheim. We did not have any basis for confirming that the hydrogen atoms in c.s.t acid are not equivalent, as is believed by Scroggie and Clark, Ralyuka, Ripan and others. All eight salts of c.s.t. acid appear as acid salts in aqueous solution. Even if the acid reaction of the first members of the series was completely understood, nothing could be said concerning the acid reaction of the latter members of the series. In this case it is completely permissible to take the point of view of Jander, who maintains that at the saturation point point of c.s.t acid a large number of hydrogen atoms may be ionized, which explains the acid reaction of solutions of the hepta- and octa-substituted salts.

However, the total number of actually existing salts of c.s.t acid at the saturation point corresponds quite accurately to its basicity, which points to the heteropoly acid theory of Miolati-Rosenheim.

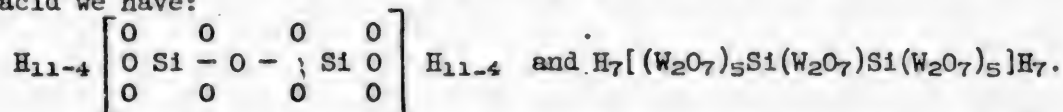
\* Calculated for  $3K_2O \cdot SiO_2 \cdot 7WO_3$ .



When we begin to substitute potassium for 9, 10, etc. hydrogen atoms, a transitional region forms between the potassium salts of the 12th and 11th series, evidently a region of their solid solutions. On the addition of 9 and 10 equivalents of KOH, solid solutions are formed still richer in salts of the 12th series; on the addition of 11, 12 and 13 equivalents of KOH the concentration of the potassium salt of 11-tungstic acid increases and then on the addition of the 14th equivalent of KOH an individual octa-substituted salt of the latter acid crystallizes.

We note that Henderson [17] synthesized the ammonium salts of silico-11-, 9- and 7-tungstic acids. We confirmed the existence of all these series by the potassium salts, first obtained by us; also by the s.t. salts of the 6th and 5th series, first synthesized by us.

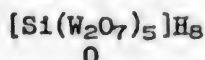
The Miolati-Rosenheim theory made it possible to predict the existence of numerous heteropoly acids not at the saturation point, and offered schemes for their structures. However, up to the present time only a very small number of these compounds have been obtained. The series of silico-tungstates we studied evidently contains the most individual representatives of this type. We will present their structural formulas in accordance with the theory of Miolati-Rosenheim and our observations. Miolati-Rosenheim treats the heteropoly acids of the 11th series as binuclear complexes with a bridge in the internal and in the external sphere; this complex is a derivative of a hypothetical hydroxy acid and is formed as a result of substitution of the oxygen atoms of its  $W_2O_7$  groups. The basicity of this acid is equal to the difference between the valence of the oxygen atoms and the valence of the complexing agent; thus, for silico-11-tungstic acid we have:



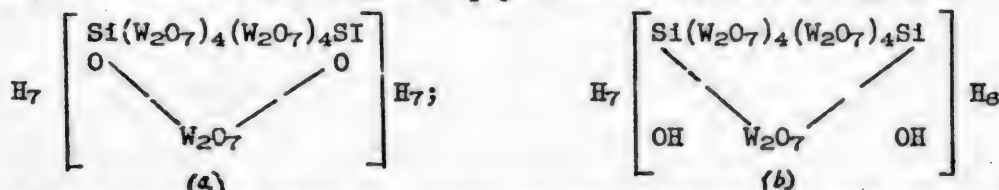
The acid should have yielded 14-substituted salts; we obtained octa-substituted potassium salts. It is possible that in salts of weaker bases the required theoretical basicity will be achieved.

We will assume the existence of a bridge only in the internal sphere, this being based on the analytical reactions of the heteropoly anion we obtained.

For silico-10-tungstic acid we obtained a hepta-substituted salt with an admixture of octa-substituted. For this series of heteropoly acids a mononuclear type of complex structure is possible.



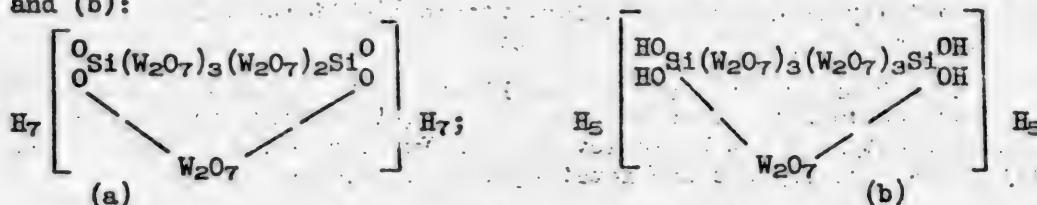
For silico-9-tungstic acid we obtained a hepta-substituted potassium salt. Silico-9-tungstic acid may be represented as a binuclear complex with a bridge in the internal sphere. The possibility of a choice between the two formulas (a) and (b) should determine further physico-chemical measurements.



In the potassium salts we synthesized the maximum basicity of the acid could not be attained. This is fully explained by the fact that the heteropoly anion is unstable and on further addition of alkali changes to a heteropoly

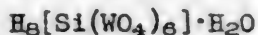
acid of a simpler structure. It is possible, however, that under other experimental conditions it may be possible to synthesize the highly-substituted salts of this series.

Silico-7-tungstic acid may be represented by the two structural formulas (a) and (b):



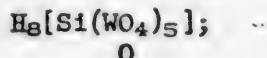
We obtained a potassium salt of this acid similar to the hexa-substituted. Possibly, by choosing a less energetic base the maximum theoretical basicity of the heteropoly acid would be attained.

For compounds of the 6th series it is most probable to consider, according to Miotati-Rosenheim, the structure to be a mononuclear complex, in which six molecules of the metallic oxide are necessary for one central atom:



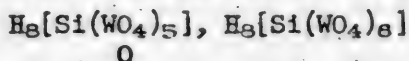
We obtained a penta-substituted salt with admixture of a quadri-substituted ( $\text{K}_{18}$ ) and a salt similar to the hexa-substituted ( $\text{K}_{19}$ ) salt of this octa-basic acid.

Compounds of the 5th series are derivatives of previous compounds, as is indicated by the proposed structural formula:



The potassium salt we obtained is a quadri-substituted salt of this acid.

Attention is drawn to the fact that silico-7-tungstic acid, belonging to a series of possible binuclear heteropoly acids, is not obtained directly, but is formed as a secondary product as a result of a slow process of polymerization of salts of heteropoly acids of a simpler series, i.e.,



and from the double salt, potassium p-tungstate and silicate. Further, if it is recalled that the potassium salt of silico-9-tungstic acid ( $\text{K}_{17}$ ) gave a solid solution of salts of the 11th and 12th series as a result of a slowly occurring transformation, it may be then stated for the first time that mononuclear and binuclear heteropoly acids are mutually transformed to the solid state.

The structure of the internal spheres of heteropoly acids is treated differently. We examined the question in detail previously [18]. It will be noted that the possibility of obtaining silico-11-, 10-, 9-, 7-, 6-, and 5-tungstates, which in turn indicates the possibility of a gradual break of a  $\text{WO}_3$  group, refutes Keggin's theory which assumes the existence, in the internal sphere, of heteropoly acid anions of the composition  $(\text{W}_3\text{O}_{10})_4$ .

For characterizing the structure of the internal spheres of heteropoly acids, the most accurate theory is evidently that of Pfeiffer, i.e. there is a coordinated  $\text{WO}_3$  group in the internal sphere. We will return to this question in more detail in our subsequent communications. The eight potassium c.s.t. salts we obtained and the entire series of potassium s.t. not at the saturation

point is very substantial proof of the theory of the structure of heteropoly acids as proposed by Miolati-Rosenheim. If it is recalled that in 1940 E.A. Nikitina had synthesized the sodium salts of phosphomolybdic and phosphotungstic acids, in which 4,5,6 and 7 hydrogen atoms were substituted by a metal, and if all the literature on highly-substituted salts is considered, then the problem of the high basicity of heteropoly acids, within the limits indicated by the Miolati-Rosenheim theory, appears to be solved.

Although wholly supporting the conception of the multibasicity of heteropoly acids, we consider it necessary to note that in several individual cases the maximum basicity may not be achieved: such as, for example, the relative instability of silicomolybdic and metatungstic acids, etc.

In certain cases the heteropoly acids may exhibit a higher basicity than would be predicted by the Miolati-Rosenheim theory, due to the ionization of the polar water molecules which are so numerous and so characteristic of the structure of these complex compounds.

It is very interesting that the decomposition products of the heteropoly acids are p-tungstates, which, according to the Miolati-Rosenheim theory, are the simplest heteropoly compounds of the same series, i.e. derivatives of the anion  $(X_nO_8)_{12-n}$ .

The results obtained enable us to confirm the idea that the coordination number of the central atom in heteropoly acids is equal to six, in accordance with the theory of Miolati-Rosenheim.

Analytical. Analysis of s.t. acid and its salts consisted in the determinations of water,  $SiO_2$ ,  $WO_3$ ,  $K_2O$  (or  $Na_2O$ ) and  $Cl'$ , and will be the subject of a special communication.

#### SUMMARY

1. Methods were developed for obtaining c.s.t acid and quadri-substituted potassium c.s.t. Potassium salts of c.s.t acid were obtained in which from one to 8 atoms of hydrogen were substituted by a metal.

2. All the potassium salts obtained have an acid reaction in water. The pH of solutions of c.s.t. acid and its potassium salts was determined.

3. Potassium salts of silico-11-, 10-, 9-, 7-, 6-, and 5-tungstic acids were obtained. Solutions of these salts have an alkaline reaction. The pH of their solutions was determined. The potassium salts of the 9,7,6 and 5th series were obtained for the first time.

4. The decomposition products of potassium silico-5-tungstates are double salts of potassium p-tungstate and silicate.

5. The potassium salts of silico-9, 6-, 5-tungstic acid are unstable and undergo transformations in the solid state.

6. The structure of c.s.t acid, its salts and all the other synthesized silicotungstates may be completely and adequately explained by the Miolati-Rosenheim theory.

7. Heteropoly acids at the saturation point are multibasic acids, evidently forming only acid salts.

8. The intraspherical substituents in heteropoly acids are most probably  $WO_3$  groups, and the coordination number of the central atoms equals six.

In conclusion, we consider it a pleasant duty to express our gratitude to

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